REMARKS

Reconsideration of this application is respectfully requested. Claims 42-45, 61, and 74 have been rewritten in independent form. Applicants respectfully submit that claims 42-45, 61, and 74 have not been amended for reasons substantially related to patentability and have not been narrowed. Claims 1-93 are pending. Because claims 1-41, 46-60, 62-73, and 75-84 have been withdrawn from consideration, only claims 42-45, 61, 74, and 85-94 are at issue.

Claims 42-45, 61, and 74 have been objected to for depending from non-elected claims. Claims 42-45, 61, and 74 have been rewritten in independent form. Accordingly, applicants respectfully request withdrawal of this objection.

Claims 88-92 have been rejected under 35 U.S.C. §112, second paragraph, as indefinite. The terms "total crystallinity" and "Rx" are allegedly vague. The term "total crystallinity" or degree of crystallinity (Xc) is well known in the art, and may be determined by known methods such as those described at page 17, line 30, to page 18, line 7, of the specification. The term "Rx" refers to reflectance, which is defined in the G. A. Smook, Handbook of Pulp & Paper Technology (p. 232) (Exhibit 1), as the ratio of the intensity of the light reflected by a paper test specimen to the intesity of light reflected by a perfectly reflecting, perfectly diffusing surface. The Rx value of a sample may be determined by known methods such as those described at page 18, lines 8-16, of the specification.

Rejection over Omiya

Claims 42-45 have been rejected under 35 U.S.C. §102(b) as anticipated by Omiya (U.S. Patent No. 4,508,894).

The Present Invention

A brief review of the chemistry and properties of cellulose and cellulose derivatives will put the invention in perspective and show how it is distinguishable from the prior art cited in the rejection. Mercerization is the swelling action of concentrated alkali, usually sodium hydroxide, on cellulose. Since cellulose is not soluble in water, the reaction is conducted as a heterogeneous reaction upon an aqueous slurry of cellulose fibers in water. The complete range of temperature and concentration conditions for mercerization with sodium hydroxide have been exhaustively studied by X-ray methods on mercerized and recovered cellulose. See Cellulose and Cellulose Derivatives, Volume V of HIGH POLYMERS, edited by Emil Ott, pages 272-345 on Mercerization, Interscience Publisher, Inc., New York, NY, 1943 (Exhibit 2). See especially, Ott at 273-274.

Very interesting is a description of changes to the microscopic structure of cellulose fibers. In a section of Ott starting at page 338 written by E. I. Valko more than fifty years ago, the changes to cotton fiber were described as follows:

> Immediately before the ripe boll burst open and exposes its flocks of cotton to the atmosphere, the fibers are tubular, with the hollow center (the "lumen") occupying a considerable portion of the cross section. No convolutions or twists are present, and the cross sections approach very closely to an elliptical or even circular form. On exposure to the air, the fiber dries out quickly and collapses to form a flat, convoluted ribbon. Commercial cotton hair is in this form.

> When the cotton hair is brought into mercerizing solution, it begins to swell at once. In a few seconds it become elliptical, and, on further swelling, the cross section becomes almost circular. The diameter of this section is at least 25 to 30% greater than the width of the collapsed fiber.[33] . . . . During the mercerization process, the cellulose of the walls swells inwardly. After the alkali treatment and during the washing and drying, the cross section shrinks. During this shrinkage, the hair retains the same circular form, but the shrinkage proceeds uniformly toward the axis and the lumen does not recover its original size. . . . . By the strong

swelling, the arrangement which was responsible for the collapse of the native hair is broken up, and the cylindrical form is retained upon subsequent drying.

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[33] M. A. Calvert and F. Summers, *J. Textile Inst.*, 16 T233 (1925).

Although many of the literature discussions of mercerization talk of it as being the treatment with alkali, it must be noted that physical studies of the effects of mercerization have all been performed on cellulose, which, after treatment with alkali, has been washed and dried. Washing removes the alkali. More recent discussions talk in terms of an irreversible change from native, amorphous cellulose I to cellulose II or crystalline cellulose.

Sarko et al. (Exhibit 3) have studied the conversion of the crystal structure of native cellulose (cellulose I) to that of cellulose II through a series of crystalline intermediate alkali cellulose complexes. See Crystalline Alkali-Cellulose Complexes as Intermediates During Mercerization by Sarko et al, page 169-177 written as Chapter 9 of The Structures of Cellulose, Rajai H. Atalla, Editor, ACS Symposium Series Volume 340, American Chemical Society, Washington, DC, 1987. "Removing the NaOH [i.e., alkali] from the structure through washing with water removes the energy-lowering electrostatic field. This results in a conversion of the structure to the only energy-lowering one that is available to it – a twofold helical, interchain hydrogen-bonded sheet structure." Sarko at page 176. While treatment with alkali to produce an alkali cellulose occurs in mercerization, it is the washing to remove the alkali which produces the final irreversible transformation to cellulose II.

> "Mercerization is the name given to the conversion accomplished by swelling native cellulose fibres in concentrated sodium hydroxide solution. Although no dissolution occurs, the swelling allows for reorganization of the chains, and cellulose II results when the swelling agent is removed." Kolpak et al., *Polymer*, 19:123-131, 123 (Feb. 1978) (Exhibit 4).

In the derivatization process to form a cellulose ether such as carboxymethyl cellulose (CMC) or methyl cellulose, the first step is the formation of an alkali cellulose, a heterogeneous reaction performed on a slurry of the starting cellulose. This is followed by derivatization (sometimes referred to as alkylation or etherification) of the cellulose, at which point it may dissolve. Derivatization performed on an alkali cellulose produced from **native cellulose (cellulose I)** is described many times in the cited references used to reject the instant claims. However, that alkali cellulose does not contain cellulose II.

In contrast, the cellulose ethers of this invention is produced by derivatization of **cellulose II**, which has been produced by mercerization and recovery of the pulp prior to formation of an alkali cellulose in the derivatization process. Therefore, the prior art processes are not the same as the claimed process, and, as the data cited below from the written description shows, the cellulose ethers of the present invention are not the same as the prior art cellulose ethers.

Omiya does not disclose or suggest preparing CMC from cellulose II (i.e., previously mercerized and recovered cellulose) as in the presently claimed invention.

Tables 1-4 below show the viscosity of CMC's prepared as described in Examples 1-5, 7, 9, and 10 of the present application from various starting cellulose pulps, including never-dried and re-wetted cellulose pulps which had been converted from cellulose I to cellulose II by mercerization and recovery. The control for each example was prepared by the same procedure as the example on the native cellulose (cellulose I) which was not mercerized and recovered before being alkalated and etherified, i.e., generally prepared by the procedure described in Wüst.

Table 1

CMC Derived from Cotton Linter Pulp				
Example No. in the present application	Concentration of NaOH (%)	1% Solution Viscosity (cP)	Control's 1% Solution Viscosity (cP)	Percentage Change in Viscosity
1 (Never-dried)[1]	14	80095	34690	130.89%
	18	83745	34690	141.41%
7 (Never-dried)	18 (Average)	79410	21493	269.47%
7 (Re-wetted dried)	18 (Average)	43453	21493	102.17%
9 (Never-dried)	18	75190	30145	149.43%
10 (Never-dried)	18	55335	25685	115.44%
10 (Never-dried)	18	57190	13920	310.85%

Table 2

CMC derived from Southern Softwood Kraft Pulp				
Example No. in the present application	Concentration of NaOH (%)	1% Solution Viscosity (cP)	Control's 1% Solution Viscosity (cP)	Percentage Change in Viscosity
2[2]	10	607	586	3.58%
	14	1268	586	116.38%
	18	1147	586	95.73%
3 (Never-dried)	7	679	550	23.45%
	10	1108	550	101.45%
	14	1365	550	148.18%
	18	1472	550	167.64%

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[1] The 7 and 10% NaOH treated pulp contained 0% sheet cellulose II and, therefore, was not mercerized.

[2] Table 2 indicates that the 7% NaOH treated pulp contained 0% sheet cellulose II and, therefore, was not mercerized..

Table 3

CMC derived from Southern Hardwood Kraft Pulp				
Example No. in the present application	Concentration of NaOH (%)	1% Solution Viscosity (cP)	Control's 1% Solution Viscosity (cP)	Percentage Change in Viscosity
5[3]	10	461	230 or 362	100.43% or 27.35%
	14	547	230 or 362	137.83% or 51.10%
	18	923	230 or 362	301.30% or 154.97%

Table 4

CMC derived from Northern Softwood Sulfite Pulp				
Example No. in the present application	Concentration of NaOH (%)	1% Solution Viscosity (cP)	Control's 1% Solution Viscosity (cP)	Percentage Change in Viscosity
4[4]	10	2037	898 or 1087	126.84% or 87.40%
	14	1835	898 or 1087	104.34% or 68.81%
	18	2608	898 or 1087	190.42% or 139.93%

Tables 1-4 show that CMC's produced by the process of the present invention have significantly higher viscosities than CMC's produced by prior art processes. For example, Table 1 shows that when a cotton linter pulp starting material is mercerized and recovered prior to alkalating and etherifying, the viscosity of the CMC formed increases by at least 102%. Table 4 shows that when a sulfite pulp starting material is mercerized and recovered prior to alkalating and etherifying, the viscosity of the CMC formed increases by at least 104%.

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[3]   Table 6 indicates that the 7% treated pulp contained only 1% sheet cellulose II.
[4]   Table 5 indicates that the 7% treated pulp contained 0% sheet cellulose II and, therefore, was not mercerized.

Since the presently claimed CMC's can have significantly higher viscosities than prior art CMC's such as that disclosed in Omiya, applicants respectfully submit that they are different than prior art CMC's, and the CMC's of this invention are not anticipated by Omiya. *In re Marosi*, 218 USPQ 289 (Fed. Cir. 1983).

Rejection over Moore

Claims 61 and 74 have been rejected under 35 U.S.C. §102(b) as anticipated by Morse (U.S. Patent No. 4,269,859). Morse discloses cellulose floc granules and a process for preparing the same (see, e.g., cols. 6 and 7).

The cellulose in Morse's cellulose floc has not previously been treated with alkali and recovered. Accordingly, it is cellulose I. In contrast, the cellulose floc of the present invention is cellulose II. As discussed above, cellulose I and cellulose II are different.

Furthermore, the cellulose floc produced by the presently claimed method can be used to produce cellulose ethers having significantly higher viscosities (as shown above) than those produced with the cellulose floc containing cellulose I, such as that in Moore.

For the foregoing reasons, Moore does not anticipate claims 61 and 74 and applicants respectfully request withdrawal of this rejection.

Rejection over Edelman

Claims 85-93 have been rejected under 35 U.S.C. §103(a) as obvious over Edelman (U.S. Patent No. 4,941,943). Edelman disclose a method for preparing CMC. The Examiner asserts that it would have been obvious to select mercerized and recovered cellulose pulp to produce sodium CMC as taught by Edelman, because Edelman had disclosed "the

mercerization of cellulose to achieve accessibility and homogeneity before the cellulose is activated with NaOH to produce [CMC]" (col. 1, lines 11-20).

Contrary to the Examiner's assertion, Edelman does not disclose or suggest mercerizing and <u>recovering</u> cellulose before converting it into CMC. At col. 1, lines 11-30, Edelman discusses the benefits of mechanically treating cellulose mixed with alkali before "the etherification itself":

> As a result of the pretreatment, i.e., the mercerization, alkali cellulose is produced, which forms NaCMC together with the etherification reagent.

(col. 1, lines 17-20).

Edelman does not disclose or suggest CMC derived from cellulose having at least about 20% by weight of cellulose II. The CMC in Edelman is derived from cellulose which has not been mercerized *and recovered*. Therefore, the cellulose used to prepare the CMC in Edelman is cellulose I, not cellulose II. As discussed above, CMC derived from cellulose I has significantly different properties than that derived from cellulose II. Accordingly, Edelman does not render obvious claims 85-87.
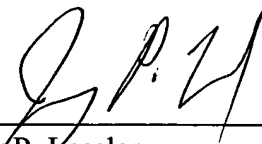
Edelman also does not disclose or suggest CMC derived from cellulose having an Rx value of greater than 0.57. Cellulose I has an Rx value less than 0.57. Since the cellulose to prepare the CMC in Edelman is cellulose I, it has an Rx value less than 0.57. Accordingly, Edelman does not render obvious claims 88-90.

Cellulose I also does not have a total crystallinity of less than about 60% or a moisture content less than 20%. Therefore, Edelman does not render obvious claims 91-93.

In view of the above remarks, it is respectfully requested that the application be reconsidered and that all pending claims be allowed and the case passed to issue.

If there are any other issues remaining which the Examiner believes could be resolved through either a Supplemental Response or an Examiner's Amendment, the Examiner is respectfully requested to contact the undersigned at the telephone number indicated below.

Respectfully submitted

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HANDBOOK OF PULP & PAPER TERMINOLOGY

A Guide To Industrial and Technological Usage

by Gary A. Smook

RANDOM ORIENTATION: Total lack of fiber alignment within a paper sheet, i.e., a sheet without grain or directionality. See also ISOTROPIC PAPER.

RANDOM VARIATION: Variation in machine-made paper properties that are neither pure machine-direction (MD) nor cross-direction (CD) in origin and cannot be measured directly. The random variation is estimated by subtracting the MD and CD components from the overall variation. Because the random variation also includes measurement and analysis errors, it is sometimes referred to as "residual variation".

RANKING: Arrangement of a series of samples in order of intensity or degree with respect to some designated attribute.

RATTLE: Crackling sound produced by shaking or crumpling a sample of paper, indicative of sheet hardness or stiffness; considered a desirable attribute for certain papers such as bonds, but objectionable in some other grades.

READABILITY: Smallest incremental difference that can be read from a test instrument. Readability can sometimes be improved by the use of a magnifying lens or vernier scale; but it is useless to have a readability that is better than the test sensitivity.

READING: Numerical value indicated on the scale, dial or digital display of a measuring instrument.

RECESSES: Minute openings in paper which are connected to one surface only. See also PORES, VOIDS.

REDUCIBLE SULFUR: Those forms of sulfur in paper or paperboard which under certain conditions can be reduced to sufide and cause tarnishing of polished metals. "Reducible" forms under test conditions include sulfide, elemental sulfur, thiosulfate and polysulfide.

REEL SAMPLE: Sample of paper taken from the reel just after manufacture. Typically, one full-width, cross-direction strip made up of several plies is taken from each finished reel for testing or reference purposes. Syn. Outturn Sample.

REFLECTANCE: Ratio of the intensity of the light reflected by a paper test specimen to the intensity of light reflected by a perfectly reflecting, perfectly diffusing surface.

REFLECTANCE METER: Generic term applied to all instruments capable of measuring the reflectance of light. Typically, it refers to an instrument for measuring the reflectance of pulp and paper sheets at two specific wave lengths, sufficient for determining brightness and opacity values. There are two major categories of refectance measuring instruments, namely diffuse and directional, referring to the illuminating and viewing geometries of the instruments. Syn. Reflectometer. See also SPECTROPHOTOMETER.

REFLECTIVITY: Reflectance of material that is sufficiently thick that an increase in thickness does not alter reflectance.

REFRACTIVITY: Ability of a material to bend light rays from a straight course, measured by its refractive index. The higher the refractivity of fillers or coating pigments used in a sheet of paper, the higher will be the scattering coefficient of the sheet.

RELATIVE HUMIDITY (of paper): Relative humidity of air that is in immediate contact with paper and closed off from any other contact (usually measured with a sword hygrometer). The equilibrium of this air is a measure of the equilibrium of the paper.

RELATIVE STABILITY (of paper): Effect of a specified heat treatment on the folding endurance of paper. This accelerated aging test infers information regarding the aging qualities of the paper.

RELAXATION: See STRESS RELAXATION.

REPEATABILITY: Difference within which two tests are expected to agree 95% of the time when testing is done by one tester on the same sample using the same apparatus under controlled conditions. See also REPRODUCIBILITY.

REPLICATES: Two or more measurements made at different times on the same sample or near-identical samples.

REPLICATION: Act of repeating a measurement or series of steps to obtain a measurement.

REPRESENTATIVE SAMPLE: Sample collected in such a manner that it has characteristics of the whole material. The designation "representative" implies that the population has been properly sampled.

REPRODUCIBILITY: Difference within which two tests are expected to agree 95% of the time when testing the same sample at different locations. The reproducibility figure includes the expected variance between testers and test instruments. See also REPEATABILITY.

RESIDUAL VARIATION: See RANDOM VARIATION.

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STRY, PHYSICS
SUBSTANCES

Newark, Del.;

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INC.

CELLULOSE
AND
CELLULOSE DERIVATIVES

A MONOGRAPH

Prepared by a Staff of Specialists
under the Editorship of

EMIL OTT

Director of Research
Hercules Powder Company
Wilmington, Delaware

HIGH POLYMERS

A SERIES OF MONOGRAPHS ON THE CHEMISTRY, PHYSICS AND TECHNOLOGY OF HIGH POLYMERIC SUBSTANCES

Volume V

Cellulose and Cellulose Derivatives

Edited by EMIL OTT

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first action of an intracrystalline swelling agent is to break those hydrogen bonds between the cellulose chains which exist along the *ab* plane of the unit cell (see Fig. 5). If the swelling agent has only one polar group which forms a bond with the hydroxyl of the cellulose chain, then the plane of the glucose unit rotates approximately 30° and forms bonds with its next neighbor in the center of the unit cell. This shifts the plane of the glucose residues from the *ab* plane to a plane bisecting the *ab* and *cb* planes so that the hydroxyl groups now lie in the 101 plane. The plane containing the van der Waals' forces is thus shifted from the 002 to the $10\bar{1}$ crystallographic plane. These van der Waals' forces are little disturbed by the entrance of the swelling agent and as a result the $10\bar{1}$ interplanar distance is not a function of the molecular size of the swelling agent. The main valence chains are held together along the (101) plane by bonds formed through the swelling agent, and as a result the 101 interplanar distance is a function of the molecular size of the swelling agent. This mechanism of swelling would explain why a swelling agent which has only one hydrogen bonding atom gives the hydrate unit cell structure upon removing the swelling agent, while those containing two hydrogen bonding atoms at each end of the swelling molecule (*e. g.*, diamines) hold the plane of the glucose unit in the *ab* plane of the unit cell and thus assist the bonds between the glucose units to reunite in a manner characteristic of the native structure when the swelling agent is removed.

(d) Mercerization

Technically, the most important of swelling phenomena is the action of sodium hydroxide on cellulose, known as mercerization. The name is derived from the fact that John Mercer in 1844 observed that if cotton, either in the form of yarn or fabric, was treated with strong sodium hydroxide, it suffered considerable shrinkage, and that its tensile strength, chemical reactivity, and dye absorption increased. Modern textile mercerization is associated with increased luster and tensile strength obtained by treating cotton under tension. The mercerizing effect may be obtained also by other alkali hydroxides, organic bases, certain salt solutions, liquid ammonia, and strong acids. In the viscose rayon industry, the term mercerization has a specialized meaning, in that it refers only to the aging of alkali cellulose, but in the textile industry mercerization usually refers to the physical aspects of the process and the resulting product. A comprehensive discussion of mercerization may be found in a recent book by Marsh.[135] The

[135] J. T. Marsh, *Mercerising*. Chapman & Hall, London, 1941.

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present discussion will be limited to the swelling action of sodium hydroxide on cellulose fibers and to the formation of alkali cellulose.

When sodium hydroxide of less than about 12% reacts with cellulose fibers at room temperature there is no change in the crystal lattice, and one is forced to conclude that the swelling below this concentration is of the intermicellar type. With increasing concentration or decreasing temperature, however, the change in the lattice shows that an intramicellar change has taken place, and it must be assumed that the interior of the crystalline cellulose has now become accessible to the alkali. It is interesting to note that the point where intramicellar swelling begins coincides with the temperature and concentration at which maximum water absorption occurs, and the point corresponds to the break in Vieweg's absorption curve.

Much work has been done on the question of whether sodium hydroxide forms a compound with or is merely absorbed by cellulose. Mercer's original observation that cotton removed alkali from solution led him to believe that a chemical combination took place, followed by decomposition of the compound on treatment with water in a manner similar to the formation of sodium ethoxide and its subsequent hydrolysis. Furthermore, it is difficult to account for the viscose reaction without assuming an alcoholate formation between cellulose and sodium hydroxide. Gladstone[136] removed the uncombined alkali from cotton by washing with alcohol, and found the compound $(C_6H_{10}O_5)_2 \cdot NaOH$. Vieweg[137] made the first quantitative measurements of the absorption of sodium hydroxide from solution and found two breaks in the curve corresponding to the compounds $(C_6H_{10}O_5)_2 \cdot NaOH$ and $(C_6H_{10}O_5)_2 \cdot 2NaOH$. Since then many workers have measured the absorption of sodium hydroxide by various techniques. Some have found evidence for compound formation while others have not. Excellent reviews of these researches may be found in the literature.[138, 139, 140] In the light of our present knowledge of swelling and cellulose structure, it is now quite certain that during mercerization both absorption and compound formation take place and that the complex phenomenon is associated with the amorphous and crystalline structure of the cellulose fiber as evidenced by x-ray analysis.

The x-ray examination of mercerization has been of two types: (1) x-ray

[136] J. H. Gladstone, *J. Chem. Soc.*, **5**, 17 (1852).
[137] W. Vieweg, *Ber.*, **40**, 3876 (1907).
[138] D. A. Clibbens, *J. Textile Inst.*, **14**, T217 (1923).
[139] W. D. Bancroft and J. B. Calkin, *Textile Research*, **4**, 119, 159 (1934).
[140] J. T. Marsh and F. C. Wood, *An Introduction to the Chemistry of Cellulose*. Chapman & Hall, London, 1938.

III.   CELLULOSE FIBERS

diagrams obtained when the alkali is left in the fibers, and (2) examination
of the fibers after removal of the alkali.   When one examines cotton after
removal of the alkali, three general types of x-ray diffraction patterns are
obtained showing either (1) native cellulose, (2) or completely mercerized
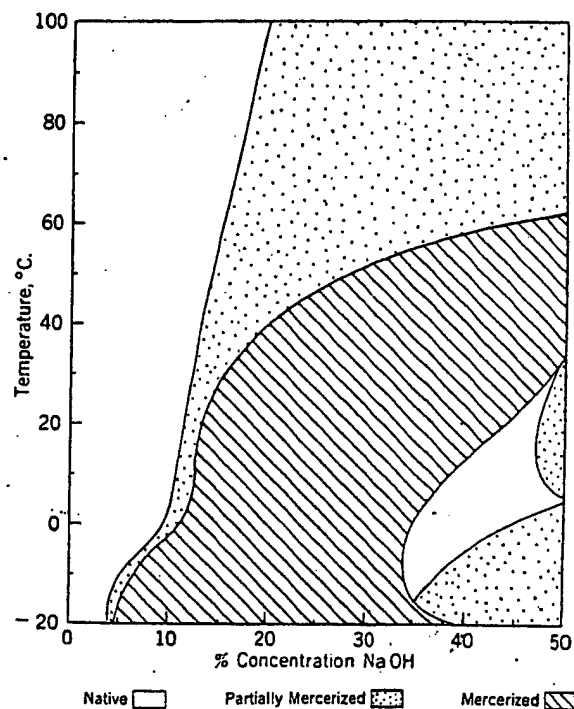cellulose, or (3) both native and mercerized cellulose.

FIG. 26.—GRAPHICAL REPRESENTATION OF THE EF-
FECT OF TREATING RAW COTTON WITH SODIUM HYDROX-
IDE AT VARIOUS TEMPERATURES AND CONCENTRATIONS
(SISSON AND SANER[141]).

The effect of temperature and concentration on the type of x-ray pat-
terns obtained for raw cotton[141] after treatment with alkali is shown in
Figure 26. Upon examining Figure 26, it is apparent that complete mer-
cerization is obtained at room temperature (20°C.) when the concentra-
tion of sodium hydroxide is above 13 to 14%. As the temperature is low-
ered, the concentration required for complete mercerization becomes in-

[141] W. A. Sisson and W. R. Saner, *J. Phys. Chem.*, **45**, 717 (1941).

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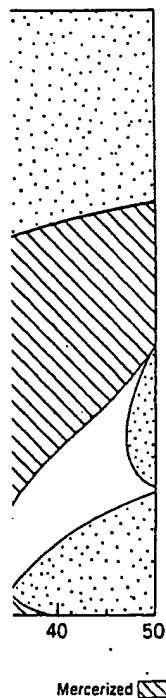mercerization becomes in-

17 (1941).

creasingly lower until, with 5% sodium hydroxide, complete mercerization is not obtained until the temperature has been lowered to about $-18°C$. With 3% sodium hydroxide there is no indication of mercerization with temperatures as low as $-70°C$. Mercerization below the freezing point of dilute sodium hydroxide solutions (3 to 13%) probably depends on the fact that ice separates out leaving behind more concentrated solutions of sodium hydroxide which are capable of mercerization.

Partial Mercerization. Preceding complete mercerization there is a certain concentration range which gives only partial mercerization. This concentration range is rather narrow between $-20°$ and $+30°C$., but becomes quite extensive at higher temperatures, until at about 65°C. it extends from approximately 16 to 50% sodium hydroxide.

At low temperatures ($-20°$ to $+30°C$.) and high concentrations (35 to 50% sodium hydroxide) the area of complete mercerization is interrupted by another area of partial mercerization. The lack of complete mercerization in this area is probably due to the formation of sodium hydroxide hydrates at these concentrations which are incapable of penetration into the crystalline cellulose lattice.

Cotton fibers containing only partially mercerized cellulose appear to be of great commercial importance, since most commercially mercerized yarns and fabrics show a mixture of native and mercerized cellulose when examined with x-rays. The variation in relative amounts of native and mercerized cellulose may be partially responsible for the variation in properties obtained by specialized commercial mercerization treatments. The ratio of native to mercerized cellulose obtained after mercerization is affected by the temperature and concentration of the mercerizing bath, the previous treatment (degradation) of the fiber, and by the presence of tension or compression on the fibers during mercerization.

At room temperature raw cotton is completely mercerized with 18% sodium hydroxide, but upon heating the mercerizing and washing bath to a higher temperature the structure is partially reverted to the native form. Thus, a mixed pattern may be obtained either from cotton treated with 18% sodium hydroxide at temperatures above 65°C., or from cotton treated first with cold 18% sodium hydroxide and then heated, either by raising the temperature of the mercerizing bath or by removing the sample from cold alkali and plunging it into boiling water. Complete mercerization, however, is obtained if the sample treated at room temperature is first washed in cold water and then plunged into boiling water, or if a sample treated above 65°C. is plunged into ice water. The apparent effect of plunging the sample into either hot or cold water is to change the tempera-

ture of the sodium hydroxide-impregnated fiber before the sodium hydroxide within the fiber is diluted to a concentration beyond which a reaction typical of the new temperature cannot take place.

X-ray studies show that the native pattern is changed to the mercerized form within a few seconds upon treatment with 18% sodium hydroxide at room temperatures. Above about 75°C. a partially mercerized pattern is obtained which gradually changes to complete mercerization after heating for days. This gradual change could be due to a slow mercerization reaction, but it appears more probable that the intracrystalline swelling attains equilibrium in a short time and that the effect of prolonged action is due to degradation. Fibers treated in the absence of oxygen with 25% NaOH at 75°C. still show partial mercerization after 15 days' treatment.

The x-ray diagram of cotton partially mercerized at room temperature indicates that the native and the mercerized cellulose exist as two separate crystalline phases. In samples which have been partially reverted at high temperatures, however, there is less definite indication of two distinctly separate crystalline phases. The two inner lines of the native x-ray pattern are not clearly resolved, which would indicate the possibility of a mixed crystallization. Partial mercerization appears to be connected in some way with fiber structure since cotton fibers cut into short sections show less partial mercerization while those ground to a fine powder show only complete mercerization.

Effect of Degradation. When cotton fibers are oxidized or hydrolyzed with acids, the area of partial mercerization is gradually decreased as degradation proceeds[141] (see Fig. 27). Furthermore, degraded fibers are more highly swollen after treatment with sodium hydroxide, especially at low temperatures and concentrations. X-ray and microscopic studies indicate that the increased swelling is largely of the intermicellar type since the degraded fibers still give the same alkali cellulose diagram as the original fibers. This increased intermicellar swelling as a result of degradation leads to dispersion in sodium hydroxide solution, which is greatest at a concentration of approximately 10% and a temperature near the freezing point.

Since degradation apparently changes the limited intermicellar swelling to the unlimited type, without affecting the nature of the intramicellar swelling, one would expect sodium hydroxide solutions of degraded cotton to consist largely of gel particles suspended in a complete molecular dispersion of degraded cellulose. This would be in keeping with the fact that weak films and fibers are always obtained with cellulose regenerated from sodium hydroxide solution, the low-viscosity continuous phase having low inherent strength. In rayons, the solubility in sodium hydroxide is ap-

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FIG. 27.—GRAPH
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The effect of tension on mercerization has been pointed out by Hess and Trogus.[142] Their experiments, which have been repeated with both sodium
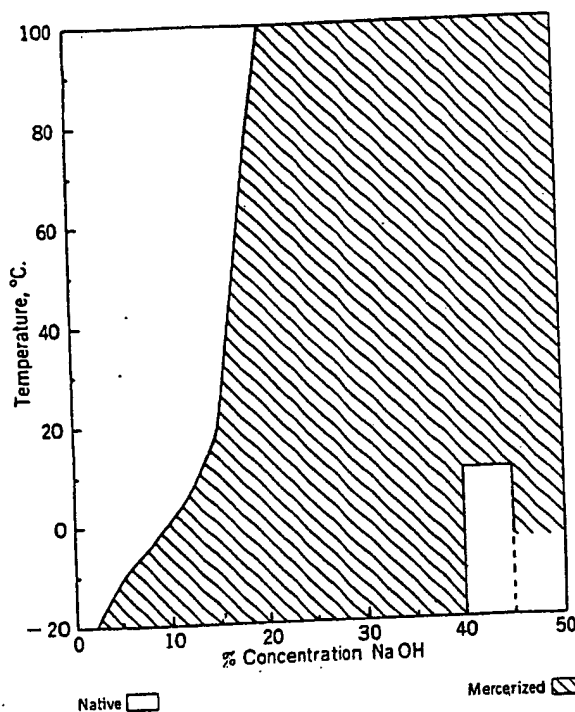

FIG. 27.—GRAPHICAL REPRESENTATION OF THE RESULTS OBTAINED WITH KIERED AND BLEACHED COTTON PRETREATED WITH 1 N HCl FOR 4 HOURS AT 75°C. BEFORE TREATMENT WITH SODIUM HYDROXIDE AT VARIOUS TEMPERATURES AND CONCENTRATIONS (SISSON AND SANER[141]).

Area in lower right-hand corner not investigated.

hydroxide and quaternary ammonium hydroxides by the author, show that intramicellar swelling may be partially prohibited by keeping the fibers under tension during the immersion in alkali, or by stretching the fibers before and during the washing out of the sodium hydroxide. When the fibers are held under tension it may be necessary to use 30 to 35% NaOH to obtain the mercerized diagram as compared with 13% in the case of un-

[142] K. Hess and C. Trogus, Z. physik. Chem., B4, 321 (1929); B11, 381 (1931).

stretched fibers, and, if sufficient tension is applied, the application of 45% NaOH for a week still gives the diagram of native cellulose if the sample is washed under tension. These and other experimental trials on the increased swelling of rubbed fibers[143] all point to the fact that any restrictive action, produced either by external forces or by the cuticle, tends to prohibit complete mercerization.

Alkali Cellulose. A great many of the investigations regarding the structure and formation of the alkali celluloses has been carried out by Hess and coworkers[134, 142, 144, 145] who examined the x-ray diagrams obtained when sodium hydroxide and other alkalies are left in the cellulose fibers. At room temperatures several soda celluloses are formed, depending upon the concentration of the alkali solution. Between a concentration of about 12 and 19% NaOH, the so-called soda cellulose I is formed which gives a definite x-ray pattern. When this is dried a further diagram is obtained of a product designated as soda cellulose III, which reverts to soda cellulose I when treated with water. Above a concentration of about 21% another diagram corresponding to a product called soda cellulose II is obtained. This does not change upon dehydration, but when sufficient water is added soda cellulose I is formed. The transition from one diagram to another does not occur sharply and mixed diagrams are obtained over a range. More recently[134] the effect of temperature and concentration has been worked out and there are indications of at least five soda celluloses. It has been emphasized[142] that water is necessary for the formation of soda cellulose I, and for the rearrangement of soda cellulose II to soda cellulose I. It has also been observed[145] that soda cellulose I, when washed with water at 100°C. and dried, gives the diagram of both native and mercerized cellulose. From the data which have been published[134] on the increased volume of the unit cell of soda celluloses I and II, it appears likely that water, as well as sodium hydroxide, enters the unit cell to form the swelling compounds. Additional information on alkali cellulose is given in Chapter VIII, D.

Most of the phenomena associated with the formation of other swelling compounds appear to hold for the formation of alkali cellulose. For example, the hydroxyl groups of the glucose units rotate into the (101) plane and the crystal lattice expands perpendicular to the (101) plane so that the cellulose chains act as lamellae in their expansion to allow room for the entrance of the sodium hydroxide and water. The intramicellar swelling

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[143] M. A. Calvert, *J. Textile Inst.*, 21, T293 (1930).

[144] C. Trogus and K. Hess, *Z. Elektrochem.*, 42, 704 (1936).

[145] K. Hess and J. Gundermann, *Ber.*, 70B, 527 (1937).

[146] W. Schramek an

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associated with the formation of alkali cellulose is strictly of the limited type and only when treated with a further reagent such as carbon disulfide does the swelling become unlimited.

Mechanism of Mercerization. As pointed out in the earlier discussion on fiber structure, x-ray and microscopic data both indicate the presence of a dual structure in a native cellulose fiber. The fiber is built up of crystalline fibrils which are separated by amorphous interfibril material. It seems logical, therefore, to assume that the over-all action of the sodium hydroxide must be considered upon the basis of its specific action upon the separate components of the fiber.

X-ray and microscopic observations made throughout the mercerization process indicate that the crystalline phase and the amorphous phase each are affected by the sodium hydroxide in a different manner.[141] X-ray diagrams show that when cotton fibers are swollen with sodium hydroxide the original native crystalline cellulose pattern disappears and that a new crystalline pattern (soda cellulose) is obtained which is characteristic of a swelling compound. At the same time, the original weak amorphous pattern is displaced by a new amorphous pattern, which is now so intense as almost to cover up the crystalline pattern. If the fibers are washed with water and dried, the pronounced amorphous pattern decreases and the crystalline pattern of the swelling compound is displaced by the pattern of mercerized cellulose. Microscopic observations in both ordinary and polarized light show that in sodium hydroxide the increase in fiber diameter is largely due to swelling of the hydrophilic interfibril material. This swelling pushes the fibrils apart and partially disarranges their original orientation with the result that the fiber increases in diameter and decreases in length, since the fibril itself is only slightly swollen but not disrupted by the treatment with sodium hydroxide.

If one considers a cellulose fiber as a two-phase system (crystalline and intercrystalline material), then it is possible to think of mercerization as a twofold reaction: (a) soda cellulose or swelling compound formation (intramicellar swelling) by the crystalline phase, and (b) alkali absorption (intermicellar swelling) by the intercrystalline or amorphous phase.

This suggested dual mechanism of mercerization would explain the lack of a true equilibrium in the system cellulose-sodium hydroxide[146] and serve as a compromise in the long-debated question as to whether cotton fibers take up sodium hydroxide by sorption or by compound formation.[140] The form of the cotton-alkali absorption curve would be in agreement with the x-ray and microscopic data, which indicate that most of the fiber swelling

[146] W. Schramek and H. Görg, *Kolloid-Beihefte*, 42, 302 (1935).

and sorption of solution is due to the pronounced swelling of the intercrystalline material. Likewise, the chemical evidence regarding compound formation is in agreement with the x-ray data, which indicate the formation of a definite swelling compound between sodium hydroxide and the crystalline cellulose at the concentration corresponding to the break in the absorption curve. The chemical reaction corresponding to alcoholate formation thus occurs in both the amorphous and crystalline areas, but with greater ease in the amorphous areas where swelling beyond soda cellulose formation occurs. On the basis of swelling experiments, Neale[147] has made a somewhat similar suggestion that the behavior of cellulose in sodium hydroxide solution can be explained on the assumption that alkali is taken up (1) according to the law of mass action to form a sodium salt, and (2) without chemical reaction in amount necessary to satisfy the Donnan equation of membrane equilibrium.

(e) Hydration

The general term hydration, as used in the literature, may refer to any of a large number of phenomena concerned with the taking up of water, the specific reference depending upon the particular phase of cellulose chemistry under discussion. The present discussion on hydration will be limited to x-ray data regarding the formation and properties of hydrate cellulose.

Swelling compounds, as a general rule, are easily decomposed by water. Upon removal of the swelling agent the fiber shrinks in diameter, and, after drying, the x-ray diagram shows the presence of a crystalline structure which differs from that of the original fiber. This regenerated structure is known as the hydrate or mercerized form, and as discussed earlier (see Fig. 5) it differs crystallographically from the native form in that the glucose residues are rotated approximately 30° around the main valence chain axes to form new interchain bonds and new interplanar distances. Hydrate cellulose has the same organic chemical structure as native cellulose but it is more reactive. This increased reactivity may be explained, partly by the geometrical arrangement of the glucose units which are farther apart and are oriented in the crystal lattice so as to make the hydroxyl groups more available, and partly by the greater proportion of amorphous areas created by the swelling or solution process which must precede the formation of a hydrate structure.

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[147] S. M. Neale, J. Textile Inst., 20, T373 (1929).

[148] S. E. Sheppa
[149] I. Sakurada
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[151] I. Sakurada
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23, 76 (Mar., 1941); *Bull. Inst.*
5, 4331 (1942).
49, 64 (1941).
1941); *Chem. Abstracts*, 36, 7304

Rayon Textile Monthly, 23, 101

racts, 36, 6075 (1942).
Abstracts, 36, 5639 (1942).
5/26, 198 (June 3, 1942); *Bull.*

); *Bull. Inst. Paper Chem.*, 13,

Ind. Eng. Chem., 34, 1429 (1942).
i., 35, 120 (1943).

D. MERCERIZATION

E. I. VALKO

Mercerization is the name used in the textile industry for the treatment of cotton yarn or fabric with concentrated aqueous caustic solution. The process dates from 1844, when John Mercer,[1] upon filtering concentrated caustic soda through a cotton cloth, observed that the cotton swelled considerably and showed somewhat modified properties even after the caustic had been removed by washing. The fabric shrank, its tensile strength increased, and it acquired a higher power to absorb dyestuffs. Caustic potash, sulfuric acid of certain concentrations, and aqueous zinc chloride were found to have the same effects on the cloth as had sodium hydroxide, and Mercer took out a patent covering the use of all of these compounds to modify the physical properties of cellulose.[2] Mercerization developed into an important industrial process following the observation of Horace Lowe, nearly half a century later, that upon treating cotton cloth with caustic soda under tension in order to prevent shrinkage, the cotton acquired a silk-like luster.[3]

The present use of the mercerizing process aims almost always at increasing the luster of cotton. The comparatively low cost of the process promoted its wide use, and mercerization has retained its place in the textile industry even after the growth of rayon manufacture, perhaps because it combines with the production of the silky luster a retention of the strength of the native fiber.

During the century which has elapsed since Mercer's discovery, several hundred scientific investigations have been carried out on mercerizing. They have substantially enriched the knowledge of fiber structure, but they have influenced industrial practice only slightly. The literature has been

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[1] E. A. Parnell, *The Life and Labours of John Mercer.* Longmans, Green & Co., London, 1886.

[2] J. Mercer, Brit. Patent 13,296 (Oct. 24, 1850).

[3] H. A. Lowe, Brit. Patent 4452 (Dec. 22, 1890).

reviewed by Clibbens,[4] Valko,[5] and Marsh,[6] and a bibliography has been compiled by Edelstein and Cady.[7]

1. Effects of Mercerization

Our knowledge of mercerization has come from the results of investigations concerned with: (a) the mechanism of the chemical interaction of cellulose and alkalies; (b) the physical changes of the fibers during the treatment with the caustic and during the subsequent washing; and (c) the permanent changes in the properties of the fibers produced by the mercerizing process. A study of all three is necessary for an understanding of the process, but, since the first two of these will be presented at length in Chapter VIII, D on "Alkali and Other Metal Derivatives of Cellulose," only a brief summary of them will be given here.

(a) Mechanism of Chemical Interaction of Cellulose and Alkalies

Cellulose combines with sodium hydroxide to form several modifications of alkali cellulose. The compounds can be quite definite, but the amount of alkali bound by a sample of cellulose, and the amount of water bound by the compounds, varies with the alkali concentration, the temperature, and other factors.

The reaction of cellulose with caustic produces heat, which has been successfully calculated by considering it to be the sum of three components: positive heat of dissociation of a weak acid; negative heat of neutralization, i. e., heat of formation of water; and negative heat of dilution of the alkali.

The cellulose-alkali compounds hydrolyze on washing with water, and the caustic can be easily and completely removed.

(b) Physical Changes of Fibers during Treatment with Caustic and during Subsequent Washing

The two important changes in the fiber during the alkali treatment are an increase in its diameter ("swelling") and a decrease in its length ("shrinking"). Both swelling and shrinking pass through maxima when plotted against alkali concentration. When sodium hydroxide is the alkali, these maxima tend to fall at the same concentration, but they do

[4] D. A. Clibbens, J. Textile Inst., 14, T217 (1923).

[5] E. Valko, Kolloidchemische Grundlagen der Textilveredlung. J. Springer, Berlin, 1937.

[6] J. T. Marsh, Mercerizing. Chapman & Hall, London, 1941.

[7] S. M. Edelstein and W. H. Cady, Am. Dyestuff Reptr., 26, P447 (1937).

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not coincide when other alkalies are used. The amount of swelling at a given alkali concentration depends greatly on the external surface of the sample. For instance, "scoured" cotton (cotton which has been boiled in dilute alkali) swells more than does raw or "gray" cotton, while "rubbed" fibers (those from which the outer layer has been removed with fine emery paper) swell even more[8] (Fig. 52). Regenerated cellulose swells the most. The swelling can be explained by three different but somewhat related theories. The first is that the fiber surface acts as a semipermeable mem-
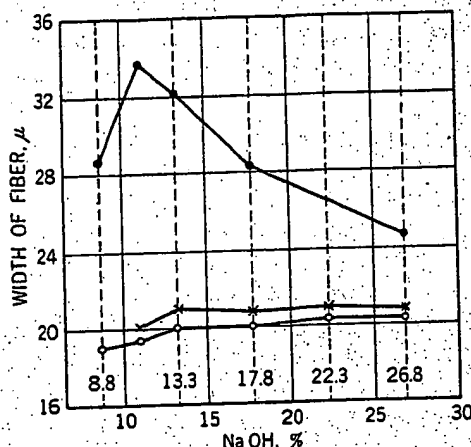
FIG. 52.—INCREASE OF THE WIDTH OF COTTON FIBERS IN NaOH SOLUTIONS (CALVERT[8]).

Lower curve: raw hairs.
Middle curve: scoured hairs.
Upper curve: rubbed hairs.

brane inside which osmotic pressure is built up as a consequence of the Donnan equilibrium or by the solution of cellulose chains in the alkali used. The second theory is that hydration of the alkali cellulose causes the effect. The third is that the swelling is caused by the electrostatic repulsion between the cellulose particles, which are charged as a result of ionization. The amount of shrinkage a fiber undergoes on mercerization is also determined to some extent by the external surface. The shrinkage can be prevented by application of tension to the fiber. Because the shrinkage remains after the alkali is washed out, in contrast to the swelling, it will be discussed below in the group of the permanent changes.

[8] M. A. Calvert, J. Textile Inst., 21, T293 (1930).

(c) Permanent Changes Produced by Mercerization in Properties of Fibers

The changes which the mercerizing process causes in cellulosic materials fall into four categories. These comprise: the changes in the cellulose molecules themselves; those produced in the intermolecular structure of cellulose crystallites; those produced in the distribution of crystallites and amorphous material in the cellulosic material; and, finally, those produced in the microscopic structure of the fibers.

Changes Produced in the Cellulose Molecules. There is no reason to assume any *structural difference between the single polymeric molecules* of native and of mercerized cellulose. The interpretations of the x-ray

TABLE 1

EFFECT OF MERCERIZING ON THE CHEMICAL PROPERTIES OF SCOURED COTTON (RIDGE, PARSONS, AND CORNER[9])

Variety	Fluidity		Copper number		Methylene blue number		Loss of wt. in alkali boil, %	
	Native	Mercerized	Native	Mercerized	Native	Mercerized	Native	Mercerized
Egyptian Sakel	3.68	3.70	0.01	0.01	1.17	0.96	1.32	1.23
Egyptian Uppers	3.38	3.34	0.01	0.01	1.10	0.95	1.20	1.31
Tanguis	3.47	3.42	0.015	0.01	1.24	1.09	0.84	1.28
Arizona	3.87	3.67	0.01	0.01	1.35	0.98	1.37	1.30
Peru Mitafifi	3.52	3.21	0.01	0.01	1.03	0.88	0.88	1.0

diagrams of the crystalline part of both modifications were carried out under the assumption that the molecular structure is the same in both. The only other possible molecular change is depolymerization. However, as was demonstrated, for instance, by Ridge, Parsons, and Corner,[9] all the properties of cotton which depend on the extent of the degradation remain essentially unchanged by the mercerizing process. Table 1 shows the results obtained on scoured cotton yarn which was mercerized with a 9 N NaOH solution. The measurements were carried out under strictly identical conditions:

Staudinger,[10] through the use of his viscosity method, found that a cotton cellulose was changed on mercerization from a degree of polymerization (D.P.) of 3000 to a D.P. of 2000. This change is inappreciable, since

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[9] B. P. Ridge, H. L. Parsons, and M. Corner, *J. Textile Inst.*, 22, T117 (1931).

[10] H. Staudinger and A. W. Sohn, *J. prakt. Chem.*, 155, 177 (1940).

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0.96	1.32	1.23	
0.95	1.20	1.31	
1.09	0.84	1.28	
0.98	1.37	1.30	
0.88	0.88	1.0	

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a depolymerization to a D.P. of 500 would still have left the mechanical properties of the cellulose practically unchanged.

Changes Produced in the Crystallites. X-ray examination of the native and of the mercerized fiber gives evidence for a change of crystalline form produced by mercerization, and it has been proved by Meyer and Baden-huizen[11, 12] and Kubo[13] that this change is reversible. The crystalline structures of native and of regenerated cellulose are, therefore, polymorphic. The question as to which form is more stable at room temperature cannot be answered as yet, but the direct transformation of mercerized into native cellulose indicates that at higher temperatures the native is the more stable form. There has been a tendency, in theoretical treatises on mer-cerization, to attribute a great significance to the transformation of the crystal forms, but it seems more correct to regard it as an interesting, yet merely accessory, phenomenon connected with the mercerizing process. There are very few properties of mercerized cellulose, and none of technical significance, for which the difference between the crystal structure of native and of mercerized cellulose could be held responsible.

Changes in Distribution of Crystallites and Amorphous Material. All of the technically important changes in fiber properties which are pro-duced by the mercerizing process, with the noteworthy exception of the most important one, the increase in luster, can be traced to two inter-micellar changes. These two changes are the decrease in the amount of crystalline material, and the change in orientation of the crystallites.

No comparative quantitative measurement of the sharpness of x-ray diagrams of native and mercerized cellulose has been reported. However, measurement of the x-ray diagrams of rayon (from regenerated cellu-lose) which is known to show the peculiarities of mercerized cellulose in an exaggerated degree, showed a decrease in the sharpness of the diffraction rings, giving a quantitative indication of a decrease in the size of the crystallites or an increase in the number of distortions or discontinuities in the lattice structure.

It was observed that the scattering was more intense and the rings were more diffuse for rayon than they were for native cellulose. This finding indicates that by the mercerizing process the amount of amorphous ma-terial is increased at the expense of the crystalline material. Further-more, the x-ray diagrams proved that when the mercerization is carried out without tension, the orientation of the crystallites decreases substan-

[11] K. H. Meyer and N. P. Badenhuizen, *Nature*, 140, 281 (1937).
[12] K. H. Meyer, L. Misch, and N. P. Badenhuizen, *Helv. Chim. Acta*, 22, 59 (1939).
[13] T. Kubo, *Kolloid-Z.*, 93, 338 (1940); *Z. physik. Chem.*, A187, 297 (1940).

III. CELLULOSE FIBERS,

tially.. When the mercerizing is carried out under tension, the degree of orientation is retained or even increased.[14]

Effects of the Decrease in Amount of Crystalline Material. The decrease in the amount of crystalline material and increased separation of the cellulose
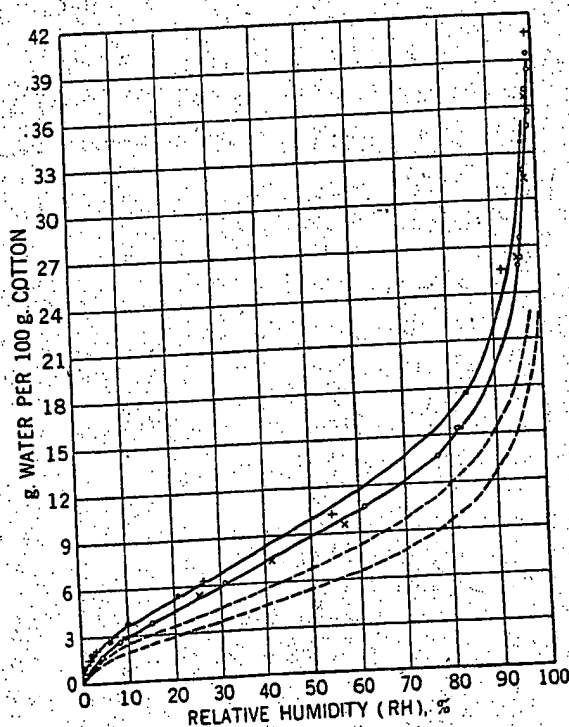

FIG. 53.—ABSORPTION OF WATER BY NATIVE AND BY MERCERIZED COTTON (URQUHART AND WILLIAMS[16]).

Curves (from top to bottom): mercerized cotton, desorption; mercerized cotton, adsorption; native cotton, desorption; native cotton, adsorption. Points refer to cotton, the mercerization of which was carried out with 15% NaOH solution; crosses refer to cotton, the mercerization of which was carried out with 28% KOH solution.

chains result in the decreased density, increased adsorption, and increased reactivity of the mercerized fibers. The density measurements were carried out by Davidson,[15] who used the pycnometric method with helium, water,

[14] G. L. Clark, *Ind. Eng. Chem.*, 22, 474 (1930).
[15] G. F. Davidson, *J. Textile Inst.*, 18, T175, T275 (1927).
[16] A. R. Urquhart and A. M. Williams, *J. Textile Inst.*, 16, T155 (1925); 18, T55 (1927).

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, 16, T155 (1925); 18, T55

and toluene as media. Results obtained are included in Table 8 (p. 407) of Section G of this chapter. The values obtained in helium were regarded as truly representing the specific volume, and, from the differences in the apparent values in helium and in water, the decrease in specific volume caused by the adsorption of water (the "contraction volume") was calculated. The average decrease was 0.018 cc. for 1 g. for scoured cotton and 0.023 cc. for 1 g. for mercerized cotton. This is in accord with the fact that mercerized cotton absorbs more water than does native cotton.

Mercer recognized that cotton becomes more hygroscopic after treatment with caustic, but exact measurements under strictly comparable conditions were carried out for the first time by Urquhart and Williams.[16] In Figure 53 are presented the percentages of water sorbed at various relative humidities by native (kier-boiled) cotton and by the same cotton after mercerization without tension. The ratio of the water contents of mercerized and native cotton is nearly constant for all relative humidities. In this particular case, the mercerized cotton takes up about 1.5 times as much water as does native cotton. The ratio depends on the concentration of the mercerizing solution and upon the tension applied during the treatment (Fig. 54).
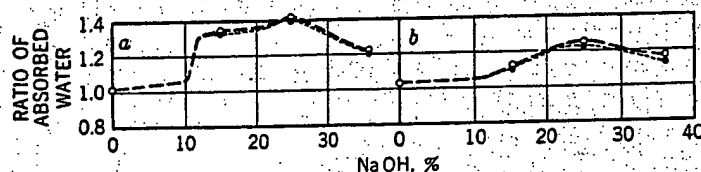
FIG. 54.—RATIO OF THE AMOUNT OF WATER ABSORBED BY COTTON WHICH WAS TREATED WITH NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS, (*a*) WITHOUT TENSION AND (*b*) UNDER TENSION, TO THE AMOUNT OF WATER ABSORBED BY UNTREATED COTTON (URQUHART AND WILLIAMS[16]).

– – – – – – Adsorption.
–·–·–·–·–· Desorption.

Another method of measuring water adsorption was used by Champetier[17] and Tankard[18] who measured the increase in concentration of an aqueous thiosulfate solution caused by the removal of water by mercerized and by native cotton which were soaked in it. They found the increase to be about twice as great for the former as for the latter.

Alkaline substances, such as sodium hydroxide, barium hydroxide, and

[17] G. Champetier, *Compt. rend.*, 195, 280 (1932).
[18] J. Tankard, *J. Textile Inst.*, 28, T263 (1937).
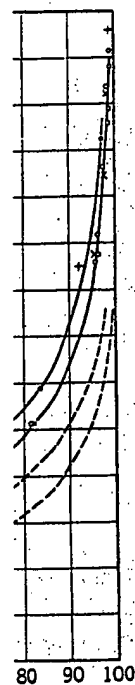
copper (from cuprammonium hydroxide), are also adsorbed from aqueous solution more strongly by mercerized cotton than by native. As the concentration of these bases increases, the difference in adsorption disappears gradually as the fiber is transformed from the native into the mercerized state. The ratio of the amounts of Na^+ ion adsorbed from 0.5 N NaOH solution by mercerized and by native cellulose, and the similar ratios of Ba^{++} ion adsorption from 0.2 N $Ba(OH)_2$ were used by Neale[19] for measuring the effects produced by mercerizing cotton under various conditions (Table 2).

TABLE 2

RATIOS OF THE ALKALI ADSORPTION OF COTTON YARN MERCERIZED WITH 25% NaOH TO THAT OF NATIVE COTTON (NEALE[19])

Cotton		Dried at room temperature		Dried at 110°C. for 6 hrs.	
		Na^+ ion ratio	Ba^{++} ion ratio	Na^+ ion ratio	Ba^{++} ion ratio
Scoured and then mercerized	Loose (about 15% shrinkage)	2.55	2.70	2.27	2.50
	Loose and restretched	2.07	2.10	1.93	1.98
	No shrinkage allowed	1.96	2.05	1.89	1.99
	Cloth mercerized loose	2.13	...	...	...
Mercerized in the "gray" state and then scoured	Loose (about 15% shrinkage)	2.09	2.20	1.84	1.97
	Loose and restretched	1.76	1.79	1.76	1.83
	No shrinkage allowed	1.68	1.73	1.69	1.75

TABLE 3

AMOUNT OF BENZOPURPURIN 4 B ADSORBED BY NATIVE COTTON AND BY COTTON TREATED WITH NaOH SOLUTIONS OF DIFFERENT STRENGTHS (KNECHT[20])

Concentration of NaOH, %	Dye adsorbed by cotton, g. per 100 g.	Concentration of NaOH, %	Dye adsorbed by cotton, g. per 100 g.
0.00	1.77	20.5	3.27
4.5	1.88	22.5	3.38
8.5	2.39	25.0	3.50
11.0	2.57	27.0	3.56
13.5	2.95	29.0	3.60
15.5	3.02	31.5	3.60
17.5	3.15		

[19] S. M. Neale, *J. Textile Inst.*, 22, T320, T349 (1931).
[20] E. Knecht, *J. Soc. Dyers Colourists*, 24, 68, 107 (1908).

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[21] A. R. Urquhart, W.
[22] J. Boulton and T. H

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E[19])

ı at room perature		Dried at 110°C. for 6 hrs.	
	Ba++ ion ratio	Na+ ion ratio	Ba++ ion ratio
ı	2.70	2.27	2.50
ı	2.10	1.93	1.98
ı	2.05	1.89	1.99
	. .	. .	. .
ı	2.20	1.84	1.97
ı	1.79	1.76	1.83
ı	1.73	1.69	1.75

COTTON AND BY COTTON
ıENGTHS (KNECHT[20])

NaOH,	Dye adsorbed by cotton, g. per 100 g.
	3.27
	3.38
	3.50
	3.56
	3.60
	3.60

Another effect of the mercerization process on the fiber is that the adsorptive power for dyes is increased. Knecht[20] investigated systematically the influence of the concentration of the mercerizing solution (Table 3), of the tension applied during the treatment (Table 4), and of the drying operation (Table 5), on dye adsorption. The effect of drying noticed here is in agreement with the observation of Urquhart, Bostock, and Eckersall[21] that the fibers exhibit a much higher sorption of water immediately after mercerizing and washing than after the subsequent drying. It can be as-

TABLE 4

AMOUNT OF BENZOPURPURIN 4 B ADSORBED BY NATIVE AND BY MERCERIZED COTTON
(KNECHT[20])

Cotton	Dye adsorbed by cotton, g. per 100 g.	
	Bleached	Unbleached
Native	1.50	1.55
Mercerized under tension	2.86	2.90
Mercerized without tension	3.54	3.39

TABLE 5

AMOUNT OF DYE ADSORBED BY COTTON (KNECHT[20])

Cotton	Dye adsorbed by cotton, g. per 100 g.	
	Benzopurpurin 4 B	Chrysophenin
Mercerized and dyed without drying	2.49	0.97
Mercerized and air-dried before dyeing	1.57	0.77
Mercerized and dried at 110°C. before dyeing	1.27	0.54
Native	0.80	0.31

sumed that the factor responsible for this phenomenon is a delayed recrystallization of part of the amorphous cellulose.

Boulton and Morton[22] found that the speed of adsorption of dyes, as measured by the time which is necessary to reach the half value of the adsorption equilibrium, is greatly increased by mercerizing. For example, two samples of raw cotton gave half-time values of 1.1 and 1.4 minutes with Sky Blue FF, a substantive dye, under the particular conditions of their experiments. After the cottons were mercerized under tension, the values were 0.25 and 0.35 minutes, respectively.

[21] A. R. Urquhart, W. Bostock, and N. Eckersall, *J. Textile Inst.*, 23, T135 (1932).
[22] J. Boulton and T. H. Morton, *J. Soc. Dyers Colourists*, 56, 145 (1940).

One view concerning dye adsorption which cannot be explained by the increase in amorphous material is that less dye is required by mercerized cotton to produce a given shade than is required by raw cotton. This opinion is held by many workers in spite of the fact that Hübner[23] dismissed the possibility some thirty years ago and that no quantitative tests have since been reported. It is not unlikely that such an effect is produced
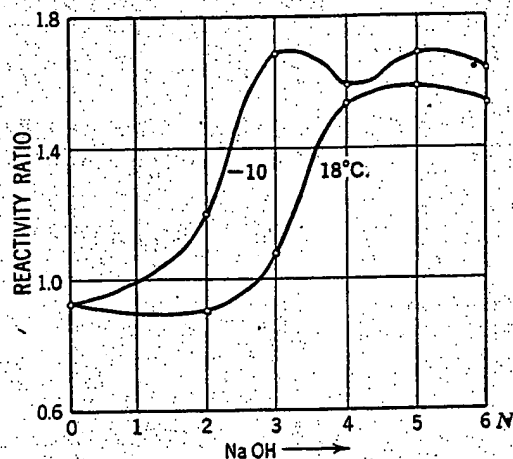
FIG. 55.—REACTIVITY RATIO OF COTTON TREATED WITH NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS AT 18°C. AND AT −10°C. TO THAT OF NATIVE COTTON (BIRTWELL, CLIBBENS, GEAKE, AND RIDGE[25]).

by the mercerization process, but the explanation for it would seem to lie in the increased luster of the fiber, which would cause a higher brilliance of the color.

The increased reactivity of mercerized cellulose, caused by the increase in amount of amorphous material, is shown by the fact that the rates of attack of hydrolyzing and oxidizing agents on it are greater than they are on native cellulose. Schwalbe[24] suggested the use of the copper number, obtained from various celluloses after treatment of 15 minutes with 5% H_2SO_4 solution, as a means of characterizing the reactivity of a fiber, and

[23] J. Hübner, J. Soc. Chem. Ind., 27, 105 (1908).
[24] C. G. Schwalbe, Z. angew. Chem., 22, 197 (1909).
[25] C. Birtwell, D. A. Clibbens, A. Geake, and B. P. Ridge, J. Textile Inst., 21, T85 (1930).

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[27] J. L. Morrison, W. B. C

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he found that this value is greatly increased by the mercerization process. Birtwell, Clibbens, Geake, and Ridge[25] used the same procedure, with the substitution of an alkaline hypobromite treatment for the sulfuric acid hydrolysis, and they obtained results illustrating the effect of the mercerizing temperature, and of the concentration of the mercerizing solution (Figs. 55 and 56).

From a thermodynamic point of view both the change in crystal structure and the increase in amorphous material during the mercerization should result in a difference in energy content between native and mercerized cellulose. Several attempts have been made to determine this energy
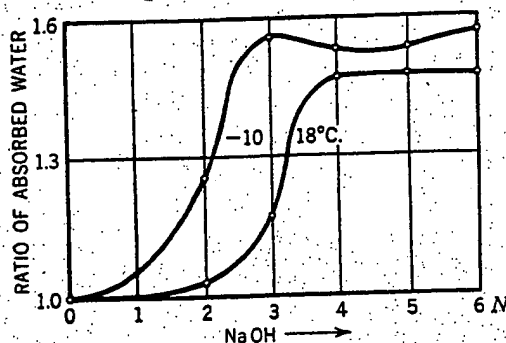
FIG. 56.—RATIO OF THE AMOUNT OF WATER ABSORBED BY COTTON WHICH WAS TREATED WITH NaOH SOLUTIONS OF VARIOUS CONCENTRATIONS AT 18°C. AND AT −10°C. TO THAT OF THE UNTREATED COTTON (BIRTWELL, CLIBBENS, GEAKE, AND RIDGE[25]).

difference. Measurement of the heats of combustion revealed no differ- ence. More successful, however, were the studies of Okamura[26] and of Morrison, Campbell, and Maass[27] based on the determination of the heat of reaction of cellulose with sodium hydroxide. At the mercerizing con- centrations of alkali, obviously, both modifications of cellulose yield the same product and the difference in the heat of reaction therefore gives the difference in the energy content. Okamura used ramie fibers (Fig. 57). With zero concentration of sodium hydroxide, i. e., with pure water, the mercerized form yielded the higher energy of wetting, a consequence of the larger "internal surface." There was very little rise in heat evolution for native ramie up to an alkali concentration of 5%, but above that concen-

[26] I. Okamura, Naturwissenschaften, 21, 393 (1933).
[27] J. L. Morrison, W. B. Campbell, and O. Maass, Can. J. Research, 18B, 168 (1940).

tration it was quite large. The heat of wetting of mercerized cellulose, on the other hand, rose rapidly with increase in alkali concentration up to 10% and then remained fairly constant up to 18%. Above 20% the difference between the heats of wetting of the native and the mercerized ramies was constant at a value even smaller than the difference between the heats of wetting in pure water. This constant difference of 1.5 cal. for each g. is, therefore, equal to the difference in energy content of the native and mercerized fibers, with the mercerized fibers having the higher energy content.
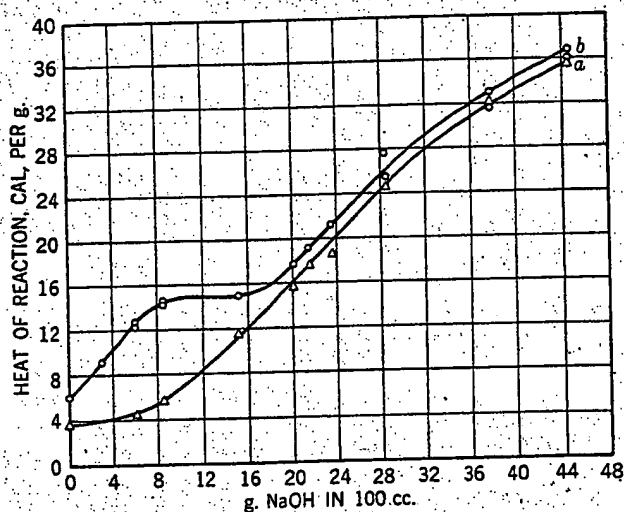
FIG. 57.—HEAT OF REACTION OF (a) NATIVE AND (b) MERCERIZED RAMIE WITH NaOH (OKAMURA[26]).

Morrison, Campbell, and Maass[27] obtained analogous results with bleached cotton, except that the energy differences were three times as large (Fig. 58). However, the absolute values of the heat evolved were also three times those for ramie, so that the ratios of the energy differences to the absolute values were practically unchanged. For bleached cotton, the energy content of the mercerized fibers was 6.6 cal. per g. higher than that of the native fibers.

Effects of the Change in Orientation of the Crystallites. If mercerization is carried out without tension, the cotton fibers shrink. Under identical conditions the extent of shrinkage depends on the tension applied. The x-ray diagram proves that by mercerization without tension the orientation of the

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cellulose crystallites decreases. With careful application of tension, the degree of orientation of native cellulose can be retained or even increased. Obviously, the shrinkage of the fiber is caused by the disorientation of the cellulose crystallites which in the native fiber are preferably aligned with their major axis nearly parallel to the fiber axis (flax, ramie) or at a steep angle to the latter (cotton).
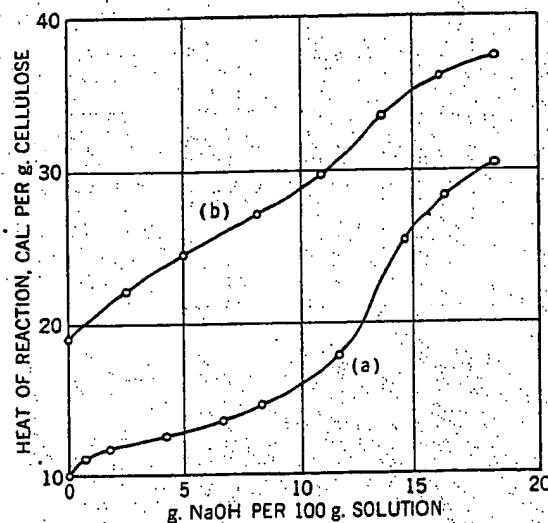
FIG. 58.—HEAT OF REACTION OF (a) NATIVE AND (b) MERCERIZED COTTON WITH NaOH (MORRISON, CAMPBELL, AND MAASS[27]).

The extent of shrinkage under identical conditions of tension varies with other factors similar to those affecting swelling: type of fiber, fiber surface characteristics, and alkali concentration.

The effect of the first factor mentioned was shown by the work of Nodder and Kinkead,[28] which showed that ramie and flax fibers contract to an even greater extent than cotton on mercerization. The smaller shrinkage of cotton is partly explained by the fact that the fibers, which are highly twisted in the native state, untwist in the alkaline solution. The removal of convolutions has itself a lengthening effect on the fibers, and the observed change in length is the resultant of this effect and of the contraction. Up to a sodium hydroxide concentration of about 8%, the effect of the

28 C. R. Nodder and R. W. Kinkead, *J. Textile Inst.*, 14, T133 (1923).

untwisting overbalances the contraction, and a lengthening of the fiber is observed.

Native, scoured, and rubbed fibers all show differences in the amount of shrinkage which they undergo on mercerization. Rubbed fibers show shrinkage even greater than that shown by scoured cotton (Fig. 59).

The effect of alkali concentration on shrinkage is similar to its effect on swelling when sodium hydroxide is used, but if other alkali hydroxides are included in the investigation, no general correlation between the shrinkage and the swelling can be established. Collins[29] carried out such experiments
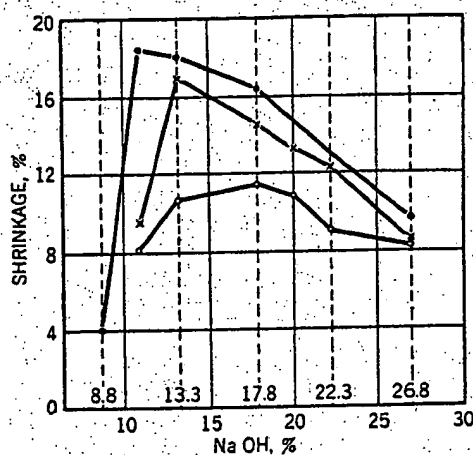
FIG. 59.—LONGITUDINAL SHRINKAGE OF COTTON FIBERS IN NaOH SOLUTIONS (CALVERT[8]).

Lower curve: raw hairs.
Middle curve: scoured hairs.
Upper curve: rubbed hairs.

with five different alkali hydroxides. His results are presented in Figure 60. The curves connect points found with increasing concentration of the hydroxides, the highest values of which are 48% NaOH, 52% KOH, 11% LiOH, 65% RbOH, and 80% CsOH. In these experiments the same fiber was exposed to alkali hydroxide solutions of increasing concentration and no maximum was observed in the shrinkage. Striking differences between the effects of the alkalies are observed when the changes in length, which correspond to an increase of, for example, 25% in the diameter of the fiber, are compared.

[29] G. E. Collins, J. Textile Inst., 16, T123 (1925).

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[30] R. O. Herzog, Ko...

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The effect of the surface layer of the fiber on the shrinkage is somewhat similar to that of the tension. This is demonstrated by the fact that, for instance, the shrinkage diagram of scoured cotton can be modified to be similar to that of raw cotton by applying tension during the alkali treatment (Fig. 61). If the tension is applied before the treatment with caustic, much less tension is required to obtain the same lowering of shrinkage
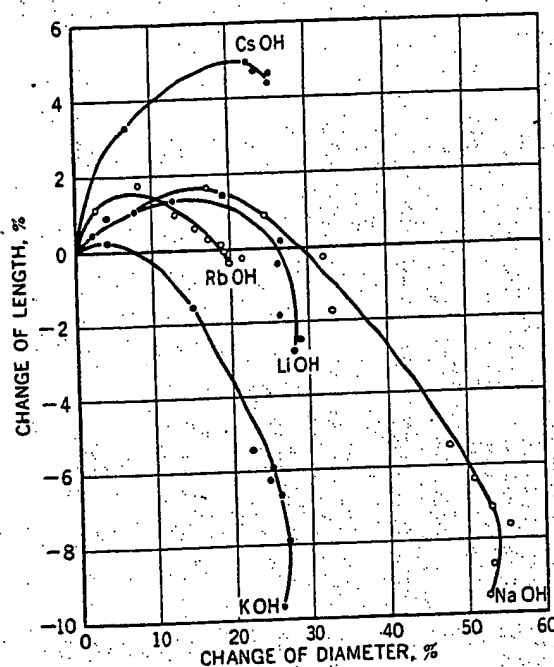
FIG. 60.—RELATIONSHIP BETWEEN THE CHANGE OF LENGTH AND THE CHANGE OF DIAMETER OF THE FIBERS IN ALKALI HYDROXIDE SOLUTIONS (COLLINS[29]).

(Fig. 62). Obviously, a state of equilibrium is not completely attained. Measurements of the absolute magnitude of the tension which is necessary to prevent shrinkage of fibers were carried out by Herzog,[30] who found that 3.8, 3.0, and 2.2 kg./mm.² prevented shrinkage when KOH, NaOH, and LiOH of 40%, 25%, and 10% concentration, respectively, were used.

The changes in orientation are reflected in the changes in the refractive

[30] R. O. Herzog, Kolloid-Z., 39, 98 (1926).

indices of fibers during mercerization. Preston[31] observed that both the transverse refractive index n_α and the axial refractive index n_γ are lowered by mercerization without tension (Table 6). He calculated from the changes in index an average angle of inclination of the crystallites to the axis of the fiber and, from the angle of inclination, the contraction which the fiber underwent during the alkali treatment. Incidentally, the fact that n_α dropped on mercerization instead of rising to approach n_γ demon-
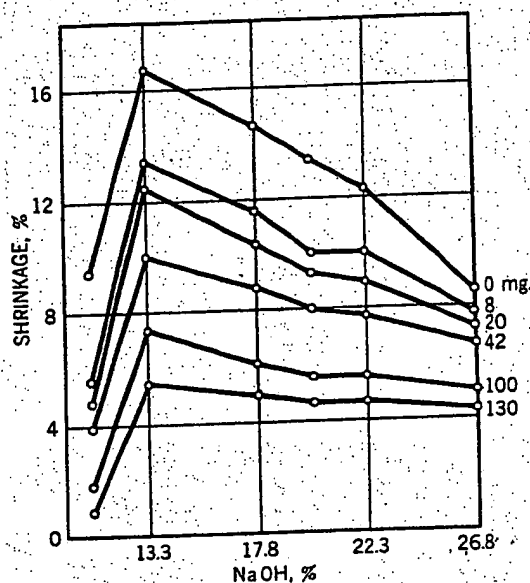
FIG. 61.—LONGITUDINAL SHRINKAGE OF SCOURED COTTON FIBERS MEASURED UNDER VARIOUS TENSIONS AFTER FREE SHRINKAGE WAS ALLOWED. (CALVERT[8]).

strated that the single crystallite of mercerized cellulose has a lower refractive index than has the single crystallite of native cotton.

The most important fiber properties which are affected by the orientation of the crystallites are breaking strength and extensibility. The extensibility of a highly oriented fiber is very small, but its breaking strength is high. In fact, Schubert[32] reported that single fibers mercerized under tension had higher breaking strengths than did native fibers (Fig. 63).

[31] J. M. Preston, Trans. Faraday Soc., 29, 65 (1933).
[32] C. Schubert, Dissertation, Dresden, 1932.

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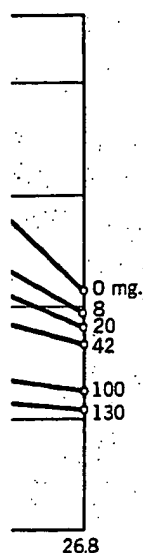
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This effect is probably due to the production of a more uniform fiber cross section by the swelling process. The claim has repeatedly been made that
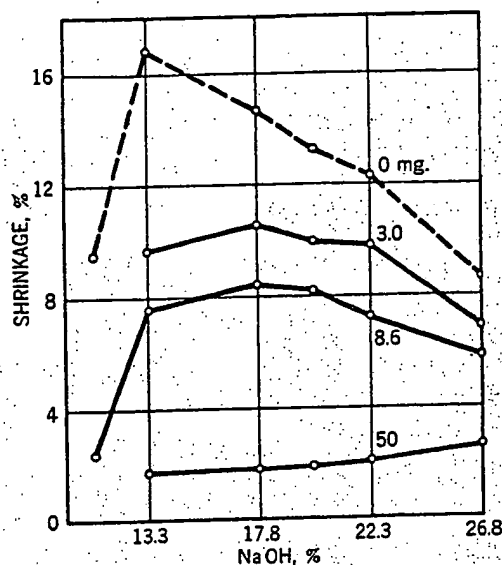
FIG. 62.—LONGITUDINAL SHRINKAGE OF SCOURED COTTON FIBERS WHEN TREATED UNDER VARIOUS TENSIONS WITH NaOH SOLUTIONS (CALVERT[8]).

TABLE 6

CHANGES IN THE REFRACTIVE INDICES OF CELLULOSE FIBERS CAUSED BY MERCERIZING (PRESTON[31])

Fiber	n_γ	n_α	$n_\gamma - n_\alpha$
Ramie and flax, native	1.596	1.528	0.068
Flax, mercerized under tension	1.571	1.517	0.054
Flax, mercerized without tension	1.556	1.518	0.038
Cotton, native	1.578	1.532	0.046
Cotton, mercerized under tension	1.586	1.522	0.044
Cotton, mercerized without tension	1.554	1.524	0.030
Lilienfeld rayon	1.559	1.515	0.044
Lilienfeld rayon, mercerized without tension	1.550	1.515	0.035

mercerizing increases the mechanical strength of fabrics and yarns also. The quantitative data on this subject are, however, contradictory.

Changes Produced in the Microscopic Structure of the Fibers. For an understanding of the increased luster (technically the most important change produced by mercerization) a study of the changes produced in the microscopic structure of the fiber is required. Immediately before the ripe boll bursts open and exposes its flocks of cotton to the atmosphere, the fibers are tubular, with the hollow center (the "lumen") occupying a considerable portion of the cross section. No convolutions or twists are present, and the cross sections approach very closely to an elliptical or even
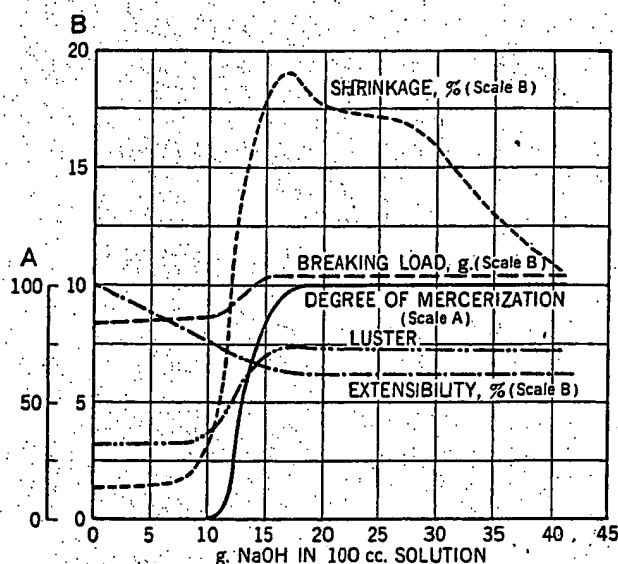
FIG. 63.—DEPENDENCE OF THE PROPERTIES OF COTTON FIBERS ON THE CONCENTRATION OF THE MERCERIZING SOLUTION (SCHUBERT[32]).

circular form. On exposure to the air, the fiber dries out quickly and collapses to form a flat, convoluted ribbon. Commercial cotton hair is in this form.

When the cotton hair is brought into a mercerizing solution, it begins to swell at once. In a few seconds it becomes elliptical, and, on further swelling, the cross section becomes almost circular. The diameter of this section is at least 25 to 30% greater than the width of the collapsed fiber.[33] These stages of the swelling are shown diagrammatically in Figure 64. During

[33] M. A. Calvert and F. Summers, *J. Textile Inst.*, 16, T233 (1925).

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There are some features of this process which are not fully understood. There was an opinion that the original circular form of the undried, ripe cotton hair was restored by mercerization. However, the lumen of the mercerized hair is filled with cellulose to an extent which is never encountered at any stage of development of the native fiber. There is obviously
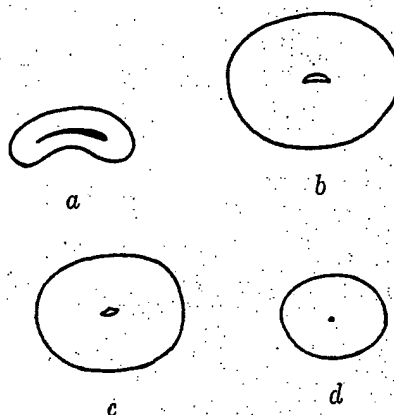
FIG. 64.—CHANGES OF THE FORM OF THE CROSS SECTION OF COTTON FIBERS DURING MERCERIZING (CALVERT AND SUMMERS[33]).

Key: (a) Fully collapsed hair.
(b) Same, swollen in 18% NaOH solution.
(c) Same, washed with water.
(d) Same, washed and dried.

some kind of organization in the native cotton fiber, possibly between the fibrils, which provokes its collapse on exposure to air. On the other hand, it seems necessary to assume that the outer wall of the fiber functions somewhat as a skin which exerts a mechanical restraint on the mercerization process and which is responsible for the cylindrical form attained during the mercerizing. By the strong swelling, the arrangement which was responsible for the collapse of the native hair is broken up, and the cylindrical form is retained upon subsequent drying.

The surface of the hair which has been treated in mercerizing solution

without tension is smoother than that of the native fiber and the con-volutions have disappeared, but, if the mercerizing is carried out under tension, the lumen is even more constricted, the transverse section is per-fectly cylindrical, and the surface is perfectly smooth. The numerous folds and indentations are completely eliminated. Obviously, drying causes a certain constriction of the skin which results in folds and creases of the surface, provided no tension is applied. By what mechanism the appli-cation of the tension during the swelling, *i. e.*, the stretching of the skin in the direction of the fiber axis at the expense of the perimeter, prevents the folding during the subsequent drying operation, is not clear. Possibly

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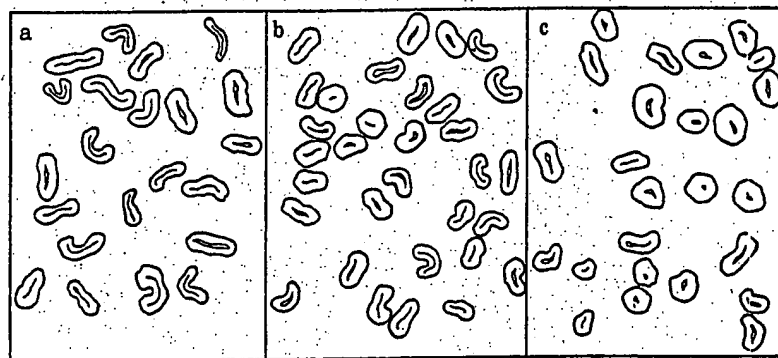
LUSTER 1

FIG. 65.—CROSS SECTIONS OF COTTON HAIRS (ADDERLEY[34]).

Key: (a)   Native cotton hairs with low luster with average ratio of length of major axis to that of minor axis equal to 2.95.
(b)   Native cotton hairs with high luster with average axis ratio of 2.00.
(c)   Mercerized cotton hairs with average axis ratio of 1.60.

peculiarities of the organization of the primary wall have a decisive role here.

Through quantitative measurements on single fibers, Adderley[34] demon-strated that the luster of cotton increases as the cross section of the hairs approaches a circular form. The correlation is a very good one, regardless of whether the cotton is mercerized or native (Figs. 65 and 66). The luster of flax and ramie, which is considerable even in the native state, is not in-creased by the mercerizing process. It seems, therefore, that the micro-scopic fiber structure is the determining factor in the amount of luster possessed by a fiber.

FIG. 66.—LUSTE
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[34] A. Adderley, *J. Textile Inst.*, 15, T195 (1924).

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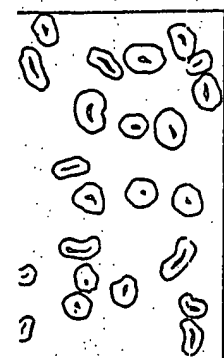
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2. Theory of Mercerization

The change in dimensions of the cellulosic fiber in the process of mercerization without tension is the resultant of two components: swelling, which occurs mainly in the transverse direction, and shrinking, which occurs in the direction of the fiber axis. The first change is reversible with washing and drying, while the second is not. That the swelling is more pronounced in the transverse direction is easily explained by the assumption that the

FIG. 66.—LUSTER NUMBER OF COTTON FIBERS AS A FUNCTION OF THE RATIO OF THE LENGTH OF THE MAJOR AXIS OF THE CROSS SECTION TO THAT OF THE MINOR AXIS (ADDERLEY[34]).

A–P: Native cotton.
Q–S: Mercerized cotton.

take-up of water occurs mostly in the transverse direction to the cellulose chains and crystallites and that the latter are preferably oriented parallel to the fiber axis. Nevertheless, the fact of contraction in length requires an explanation; because of the importance of shrinkage and tension in the mercerization process, this explanation occupies the foremost place in the theory of the mercerization.

The present knowledge of the mechanical properties of high-polymeric substances permits a derivation of such a theory. According to the ideas of

Bungenberg de Jong,[35] Hermans and de Leeuw,[36] and Kratky,[37] the crystal-line regions of the cellulose fiber are bound in a mesh of amorphous cellulosic material. In the native fiber the amorphous material is in the extended state, *i. e.*, the cellulose molecules have more or less the form of straight rods, probably as a consequence of the natural growth process. According to the theory of Meyer, von Susich, and Valko,[38] the extended chain molecules have a tendency to regain a statistically more probable configuration: that corresponding to a coil or tangle of thread. This tendency is the basis of the rubber-like elasticity of all elastomers. The elaboration of this idea in a quantitative way was furnished by Mark and his coworkers[39] and independently by Kuhn.[40] The high viscosity of the cellulosic material does not allow a contraction of the chains. The swelling in sodium hydroxide solution diminishes the friction between the chains thus allowing the contraction. Since the crystallites are suspended in the mesh of the extended chains, the contraction of these chains causes a disorientation of the crystallites.

According to the above theory, native cellulose can be compared with rubber which has been cooled under tension and, because of the high viscosity, does not contract after release of the tension until it is brought again to a certain temperature. Similar phenomena are shown by other high-polymeric substances, such as: collagen, which, when it is dry, shrinks at 90–120 °C., but when it is wet, shrinks even at 60–80 °C.[39]; and silk, which shrinks extensively on exposure to the swelling action of formic acid to give a product of rubber-like elasticity.

The fact that the shrinkage phenomenon of native cellulose fibers is not due to some peculiarity of the native fibrillar structure is demonstrated by the observation that cellophane[41] and cuprammonium rayon[42] display a completely analogous shrinkage in caustic soda solution. These materials are fixed in the extended state by the coagulation under tension during the spinning process. Bungenberg de Jong subjected cellulose xanthate in the plastic state to a stress and fixed it in the extended state by treatment with acid. He found that cellulose so obtained undergoes even in water a longitudinal contraction with a simultaneous increase in diameter.

[35] H. G. Bungenberg de Jong, *Z. physik. Chem.*, 130, 205 (1927).
[36] P. H. Hermans and A. J. de Leeuw, *Kolloid-Z.*, 81, 300 (1937).
[37] O. Kratky, *Kolloid-Z.*, 70, 14 (1935).
[38] K. H. Meyer, G. von Susich, and E. Valko, *Kolloid-Z.*, 59, 208 (1932).
[39] E. Guth and H. Mark, *Monatsh.*, 65, 93 (1934).
[40] W. Kuhn, *Kolloid-Z.*, 68, 2 (1934); 76, 258 (1936); 87, 3 (1939).
[41] G. van Iterson, Jr., *Chem. Weekblad*, 30, 2 (1933).
[42] G. Saito, *Kolloid-Beihefte*, 49, 365 (1939).

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3. Optimum Conditions for Mercerization

A determination of the optimum conditions for mercerization is of in-
terest from the commercial point of view. The properties of the mercerized
fibers which are important are luster, breaking strength, and extensibility,
while the variables which may change these properties are the time of
treatment, the temperature of treatment, the concentration of alkali, the
tension, and the previous treatment of the fibers.
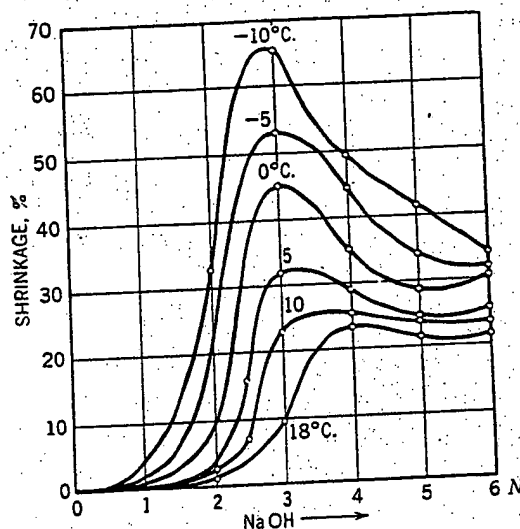
FIG. 67.—SHRINKAGE OF COTTON YARN SUF-
FERED BY TREATMENT WITH NaOH SOLUTIONS OF
VARIOUS CONCENTRATIONS AT VARIOUS TEM-
PERATURES (BIRTWELL, CLIBBENS, GEAKE, AND
RIDGE[26]).

Schubert[32] has investigated the effect of the sodium hydroxide concen-
tration. The fibers were allowed to shrink and then were stretched to their
original length before washing out the caustic soda. The shrinkage ob-
tained with the caustic soda before stretching was noted. The degree of
mercerization of the finished fiber was measured by the extent of the
change in the x-ray diagram. The results (Fig. 63) show that the breaking
strength, as well as the luster, reached its highest value at about
16% NaOH and an increase in the concentration of the alkali brought no
further change in these properties. The x-ray diagram showed that the

degree of mercerization was 100% at about 18% NaOH. The shrinkage has an optimum value at about 17% NaOH. The extensibility decreases with increasing concentration and the lower limit is reached at 16% NaOH, probably as a result of complete untwisting of the fiber.

A systematic investigation of the effect of temperature and concentration of the mercerizing solution on the properties of cotton yarn was carried out by Edelstein.[43] The temperatures were 15°C., 32°C., and 43°C., and the NaOH concentrations, 13%, 15.5%, 22.5%, and 29%. It was found, in agreement with the results of Birtwell, Clibbens, Geake, and Ridge[25] (Fig. 67), that the lower the temperature of the particular caustic solution, the greater was the tension necessary to prevent the yarn from shrinking in

TABLE 7

EFFECT OF STRETCHING DURING MERCERIZING ON THE PROPERTIES OF EGYPTIAN COTTON FIBERS* (SCHUBERT[37])

Stretched, mm.	Breaking load, g.	Extension at break, %	Luster number
0.00	9.8	16.3	4.3
1.00	9.8	11.1	5.7
1.90	10.2	9.4	6.5
2.65	10.2	6.5	7.8
3.00	10.4	5.8	7.7
3.45	10.4	5.3	7.3

* Original length 14.80 mm.; shrinkage 2.62 mm.

the solution and the greater was the dye affinity, the barium absorption ratio, and the tensile strength of the mercerized yarn. However, the effect of temperature on the mercerization was slight when caustic solutions of high concentration were used. With caustic solutions at lower concentrations, the maximum luster was reached at the lowest temperature, but, with a caustic solution of 50 to 65° Twaddell (23–30%), it was reached at a temperature of 32°C.

The effect of tension when applied after shrinkage was allowed is shown in Table 7. The optimum luster was reached when the original length was restored, but the absolute strength, per unit of diameter of fiber, increased slightly on further increase in the amount of stretching. When this absolute strength is calculated, the decrease in diameter of the fiber by the stretching is to be taken into account.

[43] S. M. Edelstein, Am. Dyestuff Reptr., 25, P458, P724 (1936); 26, P423 (1937).

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Edelstein[43] found that the greater the tension applied to the yarn in a particular caustic solution, the greater was the luster and the less was the affinity for dyes of the finished material. This holds even if the tension is much higher than that which is just necessary to prevent shrinkage. These findings do not disagree with the results of Schubert (Table 7) on single fibers, if it is taken into account that a tension which may be sufficient to prevent shrinkage of the yarn or fabric as a whole is not necessarily sufficient to prevent the shrinkage of the single fiber by slipping.

In commercial practice the fibers are generally not allowed to remain in contact with the mercerizing solution for more than a minute. It is therefore necessary to obtain a complete penetration of the fabric or yarn in this short time. This is generally achieved by using scoured (alkali-boiled) cotton. If the mercerization is carried out with raw cotton, a wetting agent must be added to the bath. These agents are surface-active substances which are stable even at the high sodium hydroxide concentration used and which lower the interface tension against the surface impurities of the fiber. The most widely used agents are higher homologs of phenol.

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ACS SYMPOSIUM SERIES 340

The Structures of Cellulose

Characterization of the Solid States

Rajai H. Atalla, EDITOR
Institute of Paper Chemistry

Developed from a symposium sponsored by
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at the 190th Meeting
of the American Chemical Society,
Chicago, Illinois,
September 8-13, 1985

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Foreword

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Contents

Chapter 9

Crystalline Alkali–Cellulose Complexes as Intermediates During Mercerization

Anatole Sarko, Hisao Nishimura[1], and Takeshi Okano[2]

Department of Chemistry and Cellulose Research Institute, College of Environmental Science and Forestry, State University of New York, Syracuse, NY 13210

During a controlled mercerization of ramie cellulose, the cellulose I crystal structure is irreversibly converted to cellulose II through several crystalline alkali-cellulose complexes. The crystal structures of three of the complexes -- Na-celluloses I, IIB, and IV -- are providing information on the characteristics of the interactions between cellulose and the Na^+ ions, on the forces operating in the formation of these structures, and on the likely mechanism of the conversion. Although the formation of secondary bonds between Na^+ ions and the hydroxyl groups of cellulose must be an important driving force in the formation of crystalline complexes, the hydrophobic attractions between cellulose chains appear to be at least as important. The transformation of the parallel-chain structure of cellulose I to an antiparallel one takes place already during the initial conversion step, from cellulose I to Na-cellulose I.

It was observed in earlier studies of controlled alkali-mercerization of ramie cellulose that the crystal structure of native cellulose is transformed to cellulose II through a series of crystalline alkali-cellulose complexes (1,2). The relationships between these "Na-celluloses" and their pathways of transformation are illustrated in Fig. 1. It has further been observed that all of the transformations are crystal-to-crystal phase changes, not involving intermediate amorphous phases. All of the experimental evidence has suggested

[1]Current address: Research Center, Daicel Chemical Industries, Ltd., Himeji, Japan
[2]Current address: Department of Forest Products, Faculty of Agriculture, University of Tokyo, Bunkyu, Tokyo, Japan

that the first conversion step -- from cellulose I to Na-cellulose I -- is apparently the step in which a transformation of the parallel-chain polarity to the antiparallel one takes place.

As shown by the x-ray diffraction diagrams reproduced in Fig. 2, the Na-celluloses exhibit a relatively high degree of crystallinity and excellent crystalline orientation. In view of this, further delineation of the transformations and the mechanism of mercerization were attempted through the crystal structure analysis of three of the complexes: Na-celluloses I, IIB, and IV. All analyses have now been nearly completed, and a preliminary account of the results is given below. The detailed descriptions of the crystal structures will be published separately after the completion of the studies.

Experimental

The methods of sample preparation, the characteristics and the probable composition of all of the complexes, and the procedures for obtaining x-ray fiber diffraction diagrams have been previously described in detail (1,2). The procedures of crystal structure analysis followed in these studies are identical to those used in previous analyses concerned with the structures of celluloses and other polysaccharides (cf., in particular, refs. 3-5). In all cases, both stereochemical and crystallographic structure refinements were carried out in parallel. The refinement of both the chain conformation and the chain packing were conducted with completely flexible chain models, using computational procedures that allow any desired structural parameter to be made a refinable variable (3). The positions of the solvent and the complexing molecules in the unit cell were explicitly considered, whenever warranted (5). Further details of the analysis and the refinement procedures will be given in reports dealing with the individual crystal structures.

Results

Na-cellulose I.   The structure of the Na-cellulose I complex, although not as crystalline as that of cellulose I, obviously shows an equally good fibrous orientation (cf. Fig. 2A). The crystal structure is described by a large, four-chain unit cell, shown in Fig. 3. It contains 8 Na$^+$ and OH$^-$ pairs of ions and probably 16 molecules of water. The chain conformation is marked by features common to all crystalline cellulose polymorphs: an approximately 10.3 Å fiber repeat, a ribbon-like, twofold helical molecular shape, and the familiar O(3)—O(5˝) and O(6)—O(2˝) intramolecular hydrogen bonds. The characteristics of the chain packing are in accord with this chain conformation, showing a stacking into sheets along two directions. The presence of NaOH and water in the crystal structure, however, obviously contributes to considerable differences between the structures of Na-cellulose I and cellulose I.

The major difference between these two crystal structures resides in the chain packing polarity. As expected from the conversion studies and the irreversibility of the cellulose I to Na-cellulose I transformation, the crystal structure of Na-cellulose I is based on antiparallel chains (cf. Fig. 3). Because of the presence of Na$^+$ ions, which apparently form secondary bonds with the cel-

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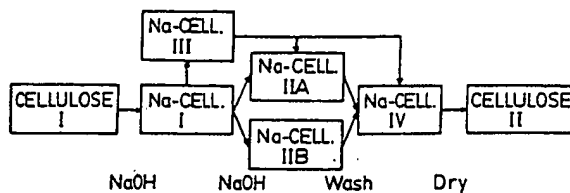8.83, b
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Fig. 1. Transformation pathways between cellulose and Na-cellulose crystal structures. (Reproduced with permission from ref. 1. Copyright 1986 John Wiley & Sons, Inc.)

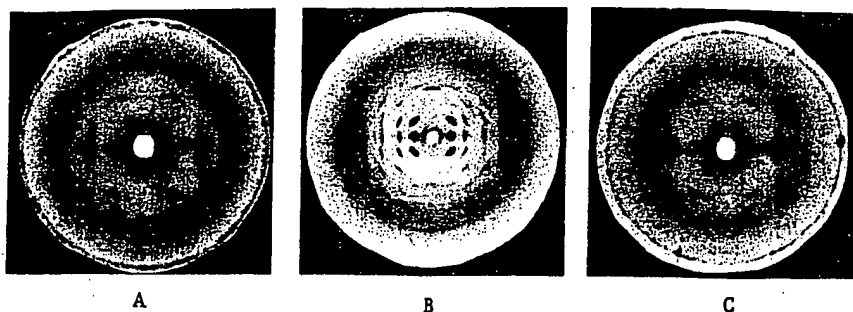Fig. 2. X-ray fiber diffraction diagrams of: (A) Na-cellulose I, (B) Na-cellulose IIB, and (C) Na-cellulose IV. (Fiber axis is vertical).
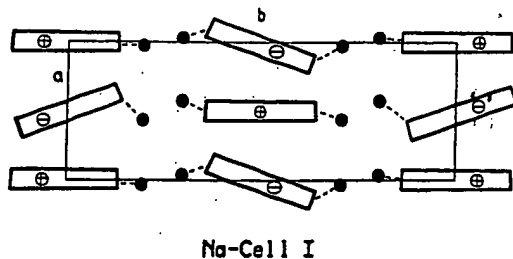

Na-Cell I

Fig. 3. The unit cell of Na-cellulose I in x-y projection: a = 8.83, b = 25.28, c (fiber axis) = 10.29 Å. The cellulose chains are shown in outline only, and filled circles indicate the positions of Na$^+$ ions. Secondary and hydrogen bonds are shown by dashed lines.

lulose hydroxyl groups, all of the interchain hydrogen bonds that
ordinarily stabilize the cellulose I structure have been broken. As
a result, distances between chains in the b direction of the unit
cell have increased and intermolecular hydrogen bonds are not pres-
ent. Nonetheless, the chains are still arranged in sheet-like struc-
tures, both along the a and b dimensions of the unit cell. It
appears that these sheet-like formations result from the ribbonlike
conformation of the cellulose molecule and, as discussed later,
hydrophobic attractions.

Na-cellulose IIB. When Na-cellulose I is allowed to absorb more
NaOH, a considerably different crystal structure results (cf. Fig.
4). The chain conformation departs from 2_1 symmetry and forms,
instead, a threefold helix. The helices pack antiparallel in a hex-
agonal fashion, with a relatively large separation distance. The
unit cell contains more than 60% of non-cellulose constituents --
NaOH and water -- surrounding each helix with a liquid-like struc-
ture. The presence of a large number of Na^+ ions quite likely
results in the formation of many secondary bonds between the cellu-
lose hydroxyls and the ions, forcing a scission of the remaining
intramolecular hydrogen bonds that are present in the Na-cellulose I
structure.
     The threefold helices of cellulose are chiral, i.e., their left-
and righthanded conformations are not identical. It is not yet known
whether the structure of Na-cellulose IIB is characterized by one
particular helix handedness, as both conformations are stable and of
not very different conformational energy. The x-ray diffraction dia-
gram (cf. Fig. 2B) is rich in detail and it should be possible to
determine the handedness of the Na-cellulose IIB helix from a
detailed x-ray refinement.

Na-cellulose IV. After all of the alkali has been washed from the
Na-cellulose IIB complex, but prior to its drying, an x-ray diffrac-
tion diagram very similar to that of cellulose II is obtained (cf.
Fig. 2C). The crystal structure of this intermediate -- Na-cellulose
IV -- is based on a two-chain, monoclinic unit cell that is indeed
very similar to that of cellulose II (cf. Fig. 5). The similarities
extend to an antiparallel chain packing and a hydrogen-bonded sheet
structure (6); the differences arise from the presence of two water
molecules in the unit cell. The water molecules are situated in
crystallographically defined positions, within the sheets composed of
corner chains, i.e., between chains of like polarity. As a conse-
quence, they participate in the hydrogen bonding linking the chains
in the b direction of the unit cell. In so doing, they lengthen the
b-axis relative to cellulose II. Although the overall pattern of
hydrogen bonds in Na-cellulose IV differs little from that in cellu-
lose II, there are some significant differences (6). For example,
because the water molecules disrupt the O(3)--O(6) intermolecular
hydrogen bonds between the corner chains, the normally tg conforma-
tion of the corner chain O(6) hydroxyls is changed to gt in Na-
cellulose IV. This evidently allows the formation of a maximum num-
ber of hydrogen bonds, as each water molecule takes part in four
hydrogen bonds. The center chains, not having any water molecules
present within the sheet, retain the gt O(6) conformations and the

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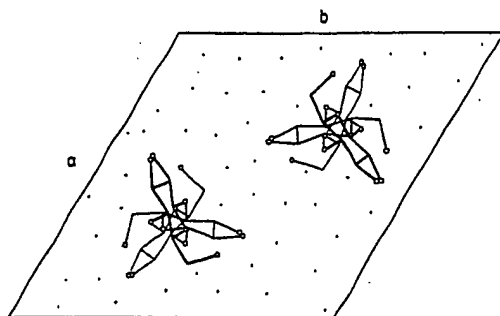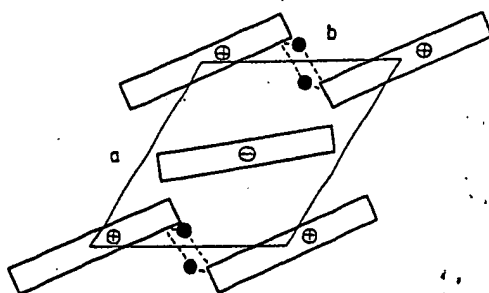

Fig. 4. The unit cell of Na-cellulose IIB in x-y projection: a = b = 14.94, c (fiber axis) = 15.39 Å, γ = 120°. The unit cell is assumed to be filled with NaOH and water. (Also see caption of Fig. 3). (Reproduced with permission from ref. 13. Copyright 1985 Gordon & Breach.)

Na-Cell IV

Fig. 5. The unit cell of Na-cellulose IV in x-y projection: a = 9.57, b = 8.72, c (fiber axis) = 10.35 Å, γ = 122°. The positions of water molecules are indicated by filled circles. (Also see caption of Fig. 3).

intermolecular hydrogen bonds that are characteristic of cellulose
II.

Discussion

From the point of view of the mechanism of mercerization, the fea-
tures of these crystal structures and their interlinking transforma-
tions support our present understanding of the process. For example,
it is known from previous studies that the conversion of cellulose I
to Na-cellulose I begins in amorphous regions of the former, and pro-
ceeds initially by converting both such regions as well as the small
crystallites (7,8). The amorphous or poorly crystalline regions of
cellulose I are of the order of 30-40 Å in lateral dimensions, as
indicated by crystallite size measurements (7). Therefore, a consid-
erable amount of cellulose I material can be converted to Na-
cellulose I before the larger crystallites are attacked. The conver-
sion thus proceeds for the most part in the presence of crystallites
of cellulose I that may exert a directing influence toward the prod-
uct that forms. The threefold helical Na-cellulose IIB is likely to
be a more stable structure relative to Na-cellulose I, but it appar-
ently is not formed in the presence of unconverted cellulose I. The
initial conversion to an alkali-complexed cellulose may, consequent-
ly, be controlled by some features of the sheet-oriented crystalline
celluloses.

The antiparallel structure of Na-cellulose I is also not sur-
prising. It is now well understood that a cellulose fiber is com-
posed of a large number of microfibrils that are essentially single
crystals in cross section. The microfibrils of cellulose I are
parallel-chain single crystals whose formation is directed by biolo-
gical processes (9). The aggregation of microfibrils into a fiber,
however, is most likely a statistically random process, resulting in
a fiber morphology that is marked by roughly equal numbers of "up"
and "down" pointing microfibrils. The majority of the non-
crystalline or amorphous regions in a cellulose I fiber may, there-
fore, be thought of as interfacial regions between microfibrils that
are randomly pointing in two directions (cf. Fig. 4 in ref. 2). A
supply of antiparallel-oriented chains is thus readily available,
leading to an antiparallel-chain crystal structure with little effort
in lateral rearrangement of chains. The presence of hydrogen-bond
breaking NaOH in considerable quantity certainly facilitates lateral
segmental motion and the resulting transformation to Na-cellulose I.
These processes and the above-described fiber morphology are schemat-
ically illustrated in Fig. 6.

Once all vestiges of an interchain hydrogen-bonded cellulose
structure have disappeared and the NaOH supply is sufficiently large,
the more stable threefold helical Na-cellulose IIB structure forms
quickly and easily. As reference to any conformational energy map of
cellulose shows (cf., for example, Fig. 2 of ref. 10), both left- and
righthanded threefold helical conformations of an isolated cellulose
chain are within the allowed region of cellulose conformations. They
are not within the minimum energy regions surrounding the twofold
helical chain because of the absence of intramolecular hydrogen
bonds. By providing a field of electrostatic attraction from the
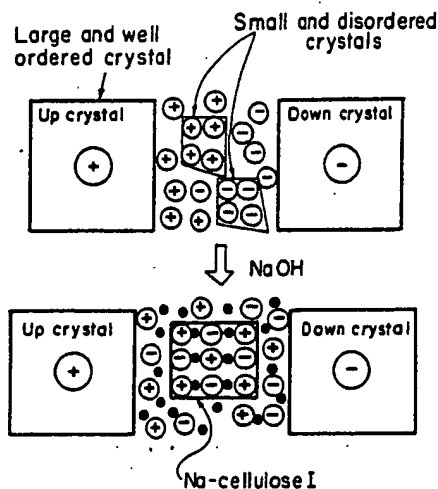surrounding Na^+ ions and the probable formation of many secondary

Fig. 6. Probable conversion of the cellulose I crystal structure to that of Na-cellulose I by the action of NaOH. Crystallites are indicated by boxed-in areas and chains by circles; + indicates "up" and – indicates "down" chain directions. The Na$^+$ ions are denoted by filled circles. (Reproduced by permission from ref. 8. Copyright 1987 John Wiley & Sons, Inc.)
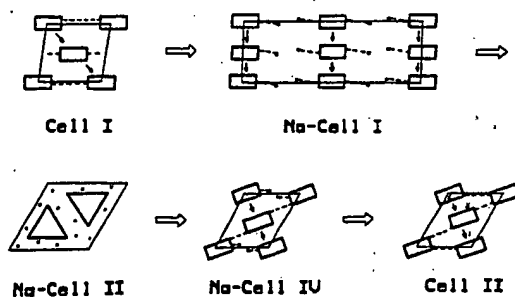

Fig. 7. A comparison of the unit cells of celluloses I and II, and Na-celluloses I, IIB, and IV, drawn roughly to scale. Arrows indicate the probable directions of hydrophobic attractions. Filled circles indicate the positions of Na$^+$ ions or water molecules. Secondary and hydrogen bonds are shown by dashed lines.

bonds between the latter and the hydroxyl groups of each glucose residue, such a conformation could become a very stable one. Its stability is probably not decreased significantly by the liquid-like surroundings of the cellulose helix in Na-cellulose IIB relative to a structure in which all Na^+ ions would be in crystallographically defined positions.

Removing the NaOH from the structure through washing with water removes the energy-lowering electrostatic field. This results in a conversion of the structure to the only energy-lowering one that is available to it -- a twofold helical, interchain hydrogen-bonded sheet structure. Because cellulose II is the most stable cellulose polymorph (10), it is not surprising that the conversion product of Na-cellulose IIB approaches it after washing. It is somewhat surprising that a hydrated structure forms at all, as it is unstable and converts readily to cellulose II upon drying. Nonetheless, it does form and its structural features suggest the presence of hydrophobic attractions that may have a bearing on all twofold helical cellulose structures.

For example, interchain hydrogen bonds could be thought of as the single dominant force in the crystallization of celluloses and Na-celluloses. Therefore, it might be expected that in Na-celluloses I and IV the Na^+ ions and the water molecules, respectively, would occupy positions between the hydrogen-bonded sheets. Instead, they disrupt the hydrogen bonds within the sheets, leaving inter-sheet contacts along the 020 (and 110, respectively) directions unchanged. Because there are no hydrogen bonds present in these planes, it is very probable that hydrophobic attractions operate along these directions, between the hydrogen-bonded sheets. Comparing the structures of celluloses I and II, and Na-celluloses I and IV, as shown in Fig. 7, reveals a common form of stacking of chains in all of these structures -- strongly suggestive of hydrophobic attractions. Other cellulose polymorphs, e.g., celluloses III_I, IV_I, and IV_{II} (not shown here), also conform to such chain stacking (11,12). Therefore, it is very probable that the aggregation of cellulose chains into various crystalline structures may primarily be governed by hydrophobic attractive forces. The only exception seems to be Na-cellulose IIB where the strong interaction between cellulose and the Na^+ ions appears to override any other forces, with the consequence that the cellulose chain adopts an unusual conformation.

Acknowledgment

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